

Equilibria and Kinetics of Interconversion of Cis and Trans Octahedral and Planar Forms of the Nickel(II) Complex of 1,4,8,11-Tetraazaundecane

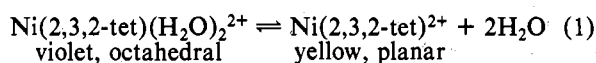
JANET D. VITIELLO and E. J. BILLO*

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When aqueous solutions of nickel(II) and 2,3,2-tet (1,4,8,11-tetraazaundecane) are mixed, the initially formed complex is predominantly the less stable *cis*-Ni(2,3,2-tet)(H₂O)₂²⁺. This complex slowly isomerizes to the trans isomer, which is in rapid equilibrium with square-planar Ni(2,3,2-tet)²⁺. The final equilibrium mixture consists of 19% *cis*, 64% *trans*, and 17% planar (0.1 M ClO₄⁻, 25 °C). Reasons for the preferential formation of the *cis* isomer are discussed. The kinetics of the *cis*-*trans* isomerization have been examined. The rate of approach to equilibrium is acid and base catalyzed, the rate law being $k_{\text{obs}} = 1.1 \times 10^{-4} + 1900[\text{H}_3\text{O}^+] + 450[\text{OH}^-]$. A mechanism is proposed. The effects of perchlorate ion concentration and of temperature on the *cis*-*trans* and *trans*-planar equilibria are examined. Increasing the perchlorate ion concentration affects the *trans*-planar equilibrium but does not appear to affect the *cis*-*trans* equilibrium. ΔH° and ΔS° for both the *cis*-*trans* and *trans*-planar interconversions have been obtained.

Introduction

Nickel(II) complexes of certain polyamine ligands produce in solution an equilibrium mixture of violet, octahedral paramagnetic NiL(H₂O)₂²⁺ and yellow, square-planar diamagnetic NiL²⁺ (L is a tetraamine ligand or two diamine ligands). One of the most extensively studied of these is the nickel(II) complex of 2,3,2-tet (1,4,8,11-tetraazaundecane, NH₂(CH₂)₂NH(CH₂)₃NH(CH₂)₂NH₂);¹ a dilute solution of this complex is about 20% planar and 80% octahedral at room temperature.^{2,3} Equilibrium 1 can be shifted toward the right



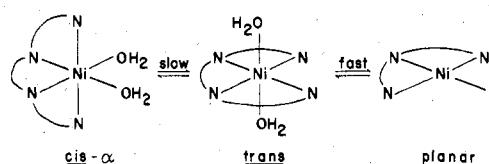
by increasing the concentration of certain background electrolytes, particularly NaClO₄, or by increasing the temperature.

The equilibrium of eq 1 is established very rapidly. It is too fast to be detectable by the conventional joule-heating temperature-jump technique⁴ but is observable with use of a laser T-jump apparatus.⁵ The speed of the planar-octahedral equilibration suggests that the interconverting species are the *trans*-diaquo and planar forms. Other chemical evidence points toward the existence of at least two octahedral isomers: when solutions of EDTA and nickel(II)-2,3,2-tet were mixed, there was an absorbance jump at 380 nm, due presumably to the rapid reaction of EDTA with *cis*-Ni(2,3,2-tet)(H₂O)₂²⁺, while the remainder of the complex, both planar and octahedral forms, reacted slowly.⁴

Recently Cook and McKenzie⁶ observed slow *cis*-*trans* isomerization of high-spin Ni(2,3,2-tet)(Me₂SO)₂²⁺ in Me₂SO. Dissolution of, for example, *trans*-Ni(2,3,2-tet)Cl₂ in Me₂SO permitted the observation of the slow isomerization of the *trans* isomer to the more stable *cis* isomer. At the same time the *trans* isomer is in rapid equilibrium with the planar form.

We wish to report our own observations on the isomerization of *cis*- and *trans*-Ni(2,3,2-tet)(H₂O)₂²⁺ in aqueous solution. We find that, in contrast to the situation in Me₂SO solvent, where the *cis* isomer is the more stable, the *trans* isomer is more stable in aqueous solution. We also made the surprising observation that, when aqueous solutions of nickel(II) and 2,3,2-tet are mixed, the initially formed complex is predom-

Scheme I



inantly *cis*-Ni(2,3,2-tet)(H₂O)₂²⁺, the less stable of the two octahedral isomers.

Experimental Section

Materials. Nickel(II) perchlorate hexahydrate was recrystallized twice from water; stock solutions were standardized by EDTA titration. 2,3,2-tet was obtained commercially (Eastman) or synthesized; both were purified by distillation at reduced pressure. Aqueous stock solutions were prepared by weight and checked by photometric titration using standard Cu²⁺ solution. Sodium perchlorate was recrystallized twice.

Crystals of orange Ni(2,3,2-tet)(ClO₄)₂ and of violet Ni(2,3,2-tet)(en)(ClO₄)₂ (caution! explosive) were prepared by mixing stoichiometric quantities of nickel perchlorate and the purified ligands in aqueous solution, adding sodium perchlorate, evaporating, and cooling. The crystals were recrystallized from hot water. Spectra of solutions of Ni(2,3,2-tet)(en)(ClO₄)₂ were identical with those of solutions prepared by mixing appropriate volumes of standard solutions of Ni²⁺, 2,3,2-tet, and en and agreed with previous work.⁷

Measurements. Spectra were recorded by using a Cary 14 spectrophotometer equipped with cell holders thermostated at 25 °C. Rates were monitored by using either a Cary 14 or Hitachi Perkin-Elmer 139 spectrophotometer or in the case of a few faster reactions using a stopped-flow spectrophotometer; all were thermostated at 25 °C. Plots of $\ln(A_\infty - A)$ vs. t were linear over several half-lives. The pH of the solution was measured at the completion of the reaction (a combination electrode filled with saturated NaCl was used for pH measurements in 2 M NaClO₄). Reaction pH was established by addition of dilute HClO₄ or dilute boric acid. In general, buffers were avoided because of the possibility of coordination to nickel(II). A slight excess of ligand was used to obtain the highest pH values. For solutions 0.1 M in NaClO₄, $-\log[\text{H}^+] = \text{pH} - 0.10$.

For temperature studies, absorbance measurements were made by using 1-cm square or 5- or 10-cm cylindrical cells in thermostated holders. Temperatures were measured by using a thermistor probe inserted into the cell.

Results and Discussion

Some time ago one of us⁸ observed that, when aqueous solutions of Ni²⁺ and 2,3,2-tet were mixed, the solution was initially violet (octahedral complex) and changed over a period of hours to the yellow-brown color characteristic of the

(1) D. F. Cook and E. D. McKenzie, *Inorg. Chim. Acta*, **31**, 59 (1978).

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(3) A. Anichini, L. Fabbrizzi, P. Paoletti, and R. M. Clay, *Inorg. Chim. Acta*, **24**, L21 (1977).

(4) R. G. Wilkins, R. Yelin, D. W. Margerum, and D. C. Weatherburn, *J. Am. Chem. Soc.*, **91**, 4326 (1969).

(5) K. J. Ivin, R. Jamison, and J. J. McGarvey, *J. Am. Chem. Soc.*, **94**, 1763 (1972).

(6) D. F. Cook and E. D. McKenzie, *Inorg. Chim. Acta*, **29**, 193 (1978).

(7) W. J. Spetnagel, Ph.D. Dissertation, New Mexico State University, Las Cruces, N.M., 1973.

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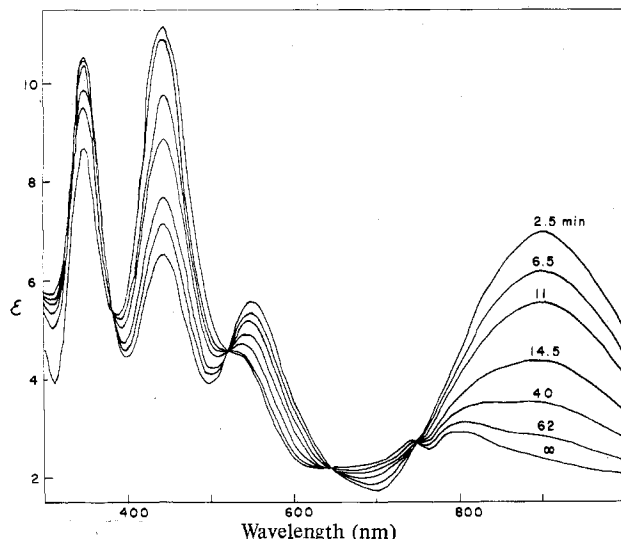
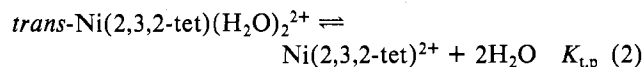
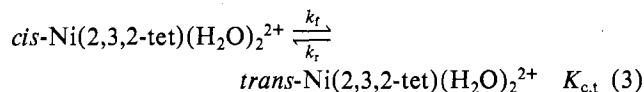


Figure 1. Spectral changes with time observed upon mixing equal volumes of 0.10 M solutions of Ni^{2+} and 2,3,2-tet (final pH 7.73).

equilibrium mixture of yellow planar and violet octahedral species. In light of the rapid equilibrium proposed to occur between the trans octahedral and planar forms⁴ (eq 2), this



observation suggested the occurrence of a slow equilibrium between cis and trans octahedral forms (eq 3) and suggested



that the initially formed octahedral species should be the cis form (Scheme I). There are two possible cis isomers, cis α and cis β ,⁹ which are not distinguishable by electronic absorption spectra.

The initial violet color was obtained irrespective of the order or method of mixing or of a slight excess of either nickel(II) or ligand. This eliminates species such as $\text{Ni}(2,3,2\text{-tet})_2^{2+}$ or $\text{Ni}_2(2,3,2\text{-tet})_3^{2+}$ as the initial violet species.

Repetitive spectral scans of the reaction are shown in Figure 1. The intensity of the near-infrared band at the beginning of the reaction and the splitting of the much less intense band at the completion of the reaction are characteristic of cis and trans isomers, respectively.¹⁰

Equilibrium Constants

The equilibrium constants $K_{t,p}$ and $K_{c,t}$ (eq 2 and 3) were evaluated by using absorbance measurements at 445 nm, the absorption of the square-planar chromophore, and at 900 nm, where spectral differences between cis and trans isomers are greatest. Absorbance measurements were made on equilibrated solutions of the complex; as well, data were obtained from many of the rate experiments described in the next section. The apparent molar absorptivity ϵ' is defined according to eq 4, where A is the absorbance, b is the path length

$$\epsilon' = A/bC_T \quad (4)$$

of the cell, and C_T is the total concentration of the nickel(II) complex. At equilibrium

$$\epsilon'_\infty = \alpha_c \epsilon_c + \alpha_t \epsilon_t + \alpha_p \epsilon_p \quad (5)$$

where the ϵ 's are the molar absorptivities of the pure cis, trans,

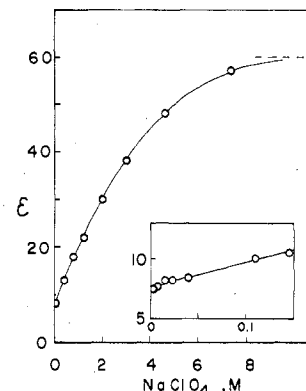
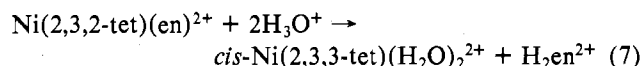


Figure 2. Effective molar absorptivity at 445 nm (square-planar band) as a function of sodium perchlorate concentration ($T = 25^\circ\text{C}$).

and planar species and α 's are the fractions of the total complex in each of the three forms, i.e., $\alpha_c = [\text{cis}]/C_T$. Also $K_{c,t} = \alpha_t/\alpha_c$ and $K_{t,p} = \alpha_p/\alpha_t$. Equation 5 leads to expression 6 for α_c ($\lambda = 900$ nm).

$$\alpha_c = \frac{\epsilon'_\infty - (1 - \alpha_p)\epsilon_t}{\epsilon_c - \epsilon_t} \quad (6)$$

The α and ϵ values were evaluated in the following manner. (i) The spectrum of the pure planar species was recorded either in 6 M NaClO_4 solutions at elevated temperatures or in nitromethane solvent. Both methods gave essentially identical spectra with $\epsilon_p = 0$ at 900 nm. At 445 nm, $\epsilon_p = 60 \pm 2 \text{ M}^{-1} \text{ cm}^{-1}$, in agreement with Cook and McKenzie.¹ (ii) Measurements at 445 nm give the concentration of the square-planar complex directly. Resolution of the adjacent octahedral bands ($\lambda_{\text{max}} = 345, 550$ nm) into Gaussian envelopes showed that the contributions of the octahedral species to the planar band at 445 nm are negligible. Thus $\alpha_p = \epsilon'/60$. Absorbance measurements on dilute solutions of complex (0.03–0.05 M) gave ϵ' values ranging from 8.5–10.5. ϵ' depends on the total $[\text{ClO}_4^-]$ as shown in Figure 2. In the experiments described here, from which K values are calculated, $[\text{ClO}_4^-]$ ranged from 0.066–0.090 M and the ionic strength from 0.10–0.15. From Figure 2, α_p would thus range from 0.15–0.16. Measurements on equilibrated solutions having $[\text{ClO}_4^-] = 0.10$ M yielded $\epsilon' = 10.0 \pm 0.5$, and thus $\alpha_p = 0.17 \pm 0.01$. Other workers have reported α_p values of 0.22 (0.10 M NaClO_4)³ and 0.15 (0.05 M in water).¹ (iii) The pure cis species was generated from the mixed-ligand complex $\text{Ni}(2,3,2\text{-tet})(\text{en})^{2+}$, in which the en must span cis positions, by pH jump from pH ~ 10 to pH 7 or lower (eq 7). Spectral studies confirmed that at pH 7



or lower dissociation was complete. The violet cis complex isomerizes to the equilibrium mixture of cis, trans, and planar; ϵ_c was obtained by extrapolation of the absorbance–time data (900 nm) to $t = 0$. For 10 experiments over the pH range 5.5–7.4, $\epsilon_c = 9.5 \pm 0.5$ and was independent of pH. [For comparison, Cook and McKenzie⁶ found $\epsilon'_\infty = 8$ for equilibrium solutions in Me_2SO , which they calculated to contain $80 \pm 5\%$ cis- $\text{Ni}(2,3,2\text{-tet})(\text{Me}_2\text{SO})_2^{2+}$. Thus $\epsilon_c = 10 \pm 0.6$. The molar absorptivity of the octahedral species thus appears to be unaffected by the change in solvent.] (iv) Dissolution of crystals of planar $\text{Ni}(2,3,2\text{-tet})(\text{ClO}_4)_2$ in water produces a solution in which equilibrium 2 is established rapidly, followed by the slow cis–trans isomerization. Initial absorbance measurements at 445 nm ($\epsilon'_0 = 11.4$) gave $\alpha_p = 0.20$, the remainder being trans. Corresponding measurements at 900 nm gave $\epsilon'_0 = 0.95 \pm 0.05$ ($N = 3$) which yield $\epsilon_t = 1.2 \pm 0.1$. (v) ϵ'_∞ values were obtained from equilibrated solutions of

(9) C. J. Hawkins, "Absolute Configuration of Metal Complexes", Wiley-Interscience, New York, 1971, p 5.

(10) L. Sacconi, *Transition Met. Chem.*, **4**, 199 (1968).

Ni(2,3,2-tet)(ClO₄)₂ (trans → cis) and from the final absorbance measurements of reactions initiated by mixing Ni²⁺ and 2,3,2-tet solutions or by pH jump of solutions of Ni(2,3,2-tet)(en)²⁺ (cis → trans). For 20 experiments over the pH range 5.5–9.8, $\epsilon'_{\infty} = 2.6 \pm 0.3$.

From eq 6 and with use of the above values, α_c is found to be 0.19 ± 0.04 and α_t is found to be 0.64 ± 0.04 . These values then lead to $K_{c,t} = 3.4 \pm 0.7$ and $K_{t,p} = 0.27 \pm 0.05$.

The same results could be obtained without the use of initial absorbance measurements at 445 nm, used in manner iv above. An iterative approach was used: ϵ_t was taken to be 0.95, and with use of ϵ_{∞} , α_p , and ϵ_c as before, approximate values of α_c and α_t were calculated. These were used to calculate an approximate $K_{t,p}$, and this in turn was used to calculate the fraction of the complex in the trans form in the solution for which $\epsilon_0 = 0.95$ at 900 nm and thus ϵ_t . After two cycles of iteration, identical ϵ_t , α_c , and α_t values were obtained.

Similar but less extensive measurements were made at $I = 2.0$ M NaClO₄. Here, $\alpha_p = 0.50 \pm 0.02$, $\alpha_c = 0.09 \pm 0.02$, $\alpha_t = 0.41 \pm 0.03$, $K_{c,t} = 4.6 \pm 1.1$, and $K_{t,p} = 1.2 \pm 0.1$. The equilibrium between cis and trans octahedral forms is essentially unaffected by the change in ionic environment, while the trans-planar equilibrium is strongly dependent on the electrolyte concentration.

Our results indicate that, at equilibrium, solutions of nickel(II)-2,3,2-tet contain largely the trans and planar forms of the complex, with the cis form accounting for approximately 20% at 25 °C. It is not clear why the trans form is predominant in H₂O while the cis predominates in Me₂SO. Solvation by the bulkier Me₂SO molecule would be expected to favor the trans isomer, yet the reverse is true. Perhaps, as suggested by Cook and McKenzie, specific hydrogen-bonded interactions stabilize one isomeric form of the octahedral cation relative to the other.

Wilkins et al. observed that, when EDTA is reacted with nickel(II)-2,3,2-tet, approximately 40% of the complex reacted immediately.⁴ This should be a measure of the cis isomer, yet we find only 19% cis. Cook and McKenzie commented on this also; they estimated that dilute solutions (0.05 M) contained approximately 10% cis and suggested, to account for the observation of Wilkins et al., that the trans form is present in both *R,R* and *R,S* forms (referring to the conformation of the secondary nitrogens) and that these react at very different rates.

We have reexamined the reaction of EDTA with equilibrated solutions of Ni(2,3,2-tet)²⁺. In agreement with Wilkins et al., we also observe an absorbance jump at 380 nm but find that it corresponds to $18 \pm 3\%$ of the total complex ($[\text{Ni}(2,3,2\text{-tet})^{2+}] = (7.1\text{--}11.6) \times 10^{-3}$ M, $[\text{EDTA}] = 0.0100$ M, pH 7.3–9.5, 0.10 M NaClO₄, 25 °C, $N = 4$), in excellent agreement with the calculated fraction in the cis form.

The fraction of cis was estimated with use of an independent method. The equilibrium constant K for the formation of the mixed-ligand complex Ni(2,3,2-tet)(en)²⁺ from Ni(2,3,2-tet)²⁺ and en was determined potentiometrically with use of procedures described in an earlier paper.¹² Because a significant fraction of the complex is in the trans form, coordination of en to Ni(2,3,2-tet)²⁺ will be less favorable than coordination of en to the similar complex Ni(trien)²⁺ which is essentially 100% cis¹. The decrease in K is a measure of the fraction of Ni(2,3,2-tet)²⁺ in the cis form; $\alpha_c = K(\text{Ni}(2,3,2\text{-tet})^{2+} + \text{en}) / K(\text{Ni}(\text{trien})^{2+} + \text{en})$. The following log K values were obtained (25 °C, 0.1 M NaClO₄): Ni(2,3,2-tet)²⁺ + en, 4.5 ± 0.1 ; Ni(trien)²⁺ + en, 5.3 ± 0.1 . Thus, $\alpha_c = 0.16 \pm 0.04$, in good agreement with the value found spectrophotometrically.

Further experiments confirming the slow equilibrium between *cis*- and *trans*-Ni(2,3,2-tet)(H₂O)₂²⁺ and the rapid

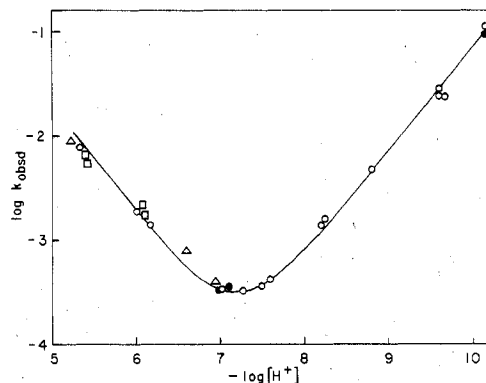


Figure 3. Hydrogen ion dependence of the observed rate of cis-trans isomerization. ($T = 25$ °C, $[\text{ClO}_4^-] = 0.1$ M, except as noted): O, reaction followed at 900 nm; ●, reaction followed at 445 nm; □, experiments using Ni(2,3,2-tet)(en)²⁺; Δ, 2 M NaClO₄.

equilibrium between *trans*-Ni(2,3,2-tet)(H₂O)₂²⁺ and planar Ni(2,3,2-tet)²⁺ involved the effect of NaClO₄. Sodium perchlorate does not affect the rate of cis-trans isomerization (Figure 3), and the absorbance at 445 nm increases slowly over a period of hours after Ni²⁺ and 2,3,2-tet solutions are mixed, as the equilibrium shifts in the direction *cis* → *trans* → planar. On the other hand, sodium perchlorate added to an equilibrated solution of the complex produces an immediate increase in absorbance at 445 nm, because the solution contains a large proportion of trans isomer. A further slight increase in absorbance then occurs over a period of hours as the small amount of cis isomer slowly isomerizes to trans.

Isomer Distribution at $t = 0$

Similar experiments were performed to determine α_c , α_t , and α_p at $t = 0$ in solutions prepared by mixing aqueous solutions of nickel(II) and 2,3,2-tet. Because of the visual observation that the solution was violet immediately upon mixing, we expected to find very little of the planar isomer and thus almost exclusively the cis isomer. However, absorbance measurements at 445 nm, extrapolated to $t = 0$ ($\epsilon'_0 = 5.9 \pm 0.1$, $N = 3$) gave $\alpha_p = 0.10 \pm 0.01$. Because of the rapid equilibrium between trans and planar, the solution must also have $\alpha_t = 0.37 \pm 0.08$. Initial absorbance measurements at 900 nm ($\epsilon'_0 = 7.2 \pm 0.3$, $N = 12$) gave $\alpha_c = 0.73 \pm 0.06$. The sum of these values is 1.20 ± 0.10 which exceeds 1.00 by more than the estimated experimental error. Because of the relatively large error produced in α_t by small errors in α_p , the calculations were performed by using the iterative method described earlier, beginning with $\alpha_p = 0$ and using $K_{t,p} = 0.27$ to calculate the distribution between planar and trans forms after α_c was obtained from eq 6. Two cycles of iteration gave $\alpha_c = 0.73 \pm 0.06$, $\alpha_t = 0.21 \pm 0.2$, and $\alpha_p = 0.06 \pm 0.02$.

It is surprising that the initially formed octahedral species is the less stable cis isomer. Such instances, of kinetic control of isomer formation, are rare in the chemistry of labile metal ions. As complexation proceeds, through stepwise formation of nickel(II)-nitrogen bonds, it appears that the 3N-bonded intermediate is predominantly facial. Closure of the final chelate ring thus leads to a 4N-bonded complex which is either *cis* α or *cis* β . Evilia, Young, and Reilly¹¹ showed that Ni(dien)(H₂O)₃²⁺ interconverts rapidly on the NMR time scale between facial and meridional isomers, with only 7% in the *mer* form. However, since chelate ring closure is much faster than ring opening, the coordination of the 3N-bonded intermediate(s) will not be determined by the equilibrium energetics of *mer* vs. *fac* coordination but rather by perhaps more subtle steric effects which influence the geometry at the moment of coordinate bond formation. The geometry is then "locked in" by coordination of the fourth nitrogen donor. If the 3N-bonded

Table I. Thermodynamic Parameters for the Blue-to-Yellow Equilibrium of Two Nickel(II) Tetraamine Complexes^a

equilibrium	ΔG° , kcal/mol	ΔH° , kcal/mol	ΔS° , cal/(deg mol)
Ni(2,3,2-tet) ²⁺			
trans \rightleftharpoons planar	0.8	5.5 \pm 0.2	16 \pm 1
cis \rightleftharpoons trans	-0.8	-2.4 \pm 0.2	-5 \pm 1
octahedral \rightleftharpoons planar ^{b,c}	0.7	3.4	9
Ni(cyclam) ²⁺			
trans \rightleftharpoons planar	-0.65	5.0 \pm 0.2	19 \pm 1
trans \rightleftharpoons planar ^c	-0.5	5.4	20

^a In 0.1 M NaClO₄ at 25 °C. ^b Reference 2. ^c Reference 3.

intermediate were *mer*, the cis isomer formed by coordination of the final nitrogen donor would be cis β , and we expect the rate of cis β -trans conversion to be rapid, as in the comparable *fac-mer* interconversion of Ni(dien)²⁺.¹¹ As well, kinetic evidence (vide infra) suggests that the cis isomer is cis α .

It is interesting to note that the initial percentages of cis and trans isomers are qualitatively in accord with the proportions which would be determined by random coordination. There are, after initial bidentate coordination, seven possible ways to coordinate the third and fourth nitrogen donors, only one of which gives trans.

The degree of protonation of the ligand does not appear to affect the cis-trans distribution. Over the pH range 6-10, 2,3,2-tet varies from predominantly H₄L⁴⁺ to predominantly HL⁺ (the protonation constants are 10.25, 9.50, 7.28, 6.02¹²). However, there was no significant change in ϵ'_0 at 900 nm over this range, indicating that protonation of nitrogen donors does not affect the initial cis-trans distribution.

Temperature Studies

The ΔH° and ΔS° for the "blue-to-yellow" interconversion of nickel(II) complexes of several tetraamine ligands have been determined.^{2,3,13} The equilibrium studied in these cases is (cis + trans octahedral) \rightleftharpoons planar. The ΔH° and ΔS° values, therefore, describe the process of cis-trans isomerization as well as the trans octahedral \rightleftharpoons planar interconversion. We have performed temperature studies of the equilibria using absorbance measurements at 900 and 445 nm over the temperature range 20-60 °C and have calculated $K_{c,t}$ and $K_{i,p}$ at each temperature. Plots of $\ln K$ vs. $1/T$ were linear, with correlation coefficients generally 0.99 or better; for the cis-trans isomerization, where absorbance changes were small, the correlation coefficient was 0.97. The results are shown in Table I.

Fabrizzi¹³ estimated that the release of a coordinated water molecule from octahedral NiL(H₂O)₂²⁺ complexes to yield planar NiL²⁺ should give rise to a ΔS° of 8-10 cal K⁻¹ mol⁻¹. Hinz and Margerum² calculated a somewhat smaller value, 7.3 cal K⁻¹ mol⁻¹/water molecule. Thus liberation of two water molecules (eq 2) would have a ΔS° of 15-20 cal K⁻¹ mol⁻¹. For explanation of the much lower ΔS° values found for Ni(2,3,2-tet)²⁺ (9 cal K⁻¹ mol⁻¹)^{2,3} and for complexes of other linear tetraamines, both groups suggested that the planar complex is not completely free of axial solvation. Table I shows, however, that when the trans-planar equilibrium is evaluated separately, ΔS° falls within the expected range. Results for Ni(cyclam)²⁺, where the octahedral complex is trans, are shown for comparison.³ We also note that the ΔH° values for the trans-planar equilibrium are closely similar.

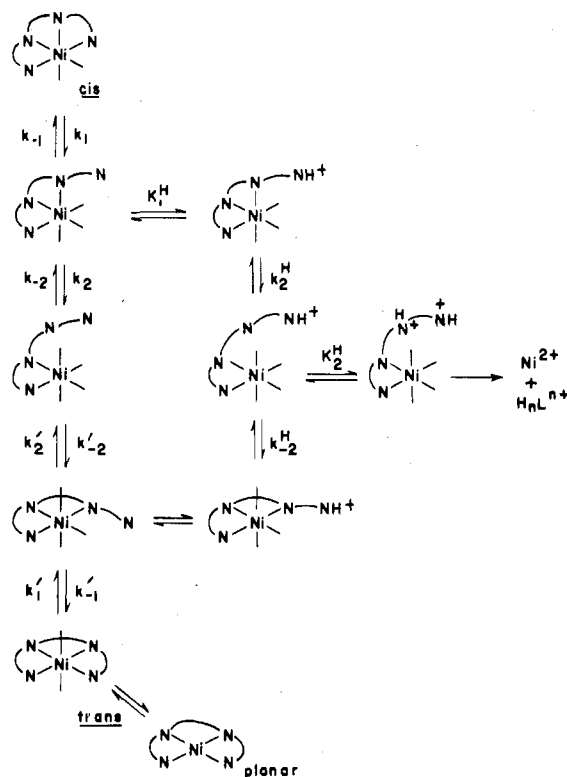


Figure 4. Proposed reaction mechanism showing the cis-trans isomerization of Ni(2,3,2-tet)(H₂O)₂²⁺ (top to bottom) and acid dissociation (left to right).

Kinetics of Cis-Trans Isomerization

Rates of approach to equilibrium were generally followed at 900 nm; a few rates were monitored at 445 nm. Equilibrium was approached beginning with the cis isomer (pH jump of Ni(2,3,2-tet)(en)²⁺) or a mixture containing predominantly the cis isomer (mixing of solutions of Ni²⁺ and 2,3,2-tet) or, in a few cases, beginning with the trans isomer (dissolution of planar Ni(2,3,2-tet)(ClO₄)₂). Results obtained from the three methods agreed within experimental error, although the absorbance changes in the third method were small, leading to relatively large uncertainties in the rate constants.

The rate data are shown in Figure 3. The reaction is acid and base catalyzed; over the pH range 5-10, k_{obsd} is given by eq 8. Rate constants were unaffected by changing the per-

$$k_{\text{obsd}} = k_0 + k_H[H_3O^+] + k_{OH}[OH^-] \quad (8)$$

chlorate ion concentration, at least between 0.07 and 2 M. The data taken at 0.1 M ClO₄⁻ were used to establish the coefficients for eq 8: $k_0 = 1.1 \times 10^{-4} \text{ s}^{-1}$, $k_H = 1900 \text{ M}^{-1} \text{ s}^{-1}$, and $k_{OH} = 450 \text{ M}^{-1} \text{ s}^{-1}$.

Rate constants for 2 M NaClO₄, for which the calculation of hydrogen ion concentrations from pH measurements is much less certain, are in good agreement, as shown in Figure 3.

Since the isomerization approaches an equilibrium rather than going to completion and the reaction is first order in both forward and reverse directions (eq 3), the first-order plots yield eq 9 from which $k_r = k_{\text{obsd}}/(1 + K_{c,t})$. With $K_{c,t} = 3.4 \pm 0.7$, $k_r = (0.23 \pm 0.03)k_{\text{obsd}}$ and $k_f = (0.77 \pm 0.03)k_{\text{obsd}}$.

$$k_{\text{obsd}} = k_f + k_r \quad (9)$$

The mechanism proposed for the acid-catalyzed isomerization is shown in Figure 4. The cis α form is shown, although there is no direct evidence that this is the cis form of the complex. The ligand partially unwraps, by successive dissociations of a terminal N followed by a secondary N. Both of the dissociated species are in rapid equilibrium with protons.

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[We estimate the protonation constant of the terminal amino group to be 10^7 , by analogy with the second protonation constant of en, following the assumption that Ni^{2+} has the same effect as H^+ . We estimate the second protonation constant to be 10^6 , by analogy with $\log K_4^{\text{H}}$ of 2,3,2-tet.] Rapid ring closures form successively the 3N-bonded and 4N-bonded complex.

The acid-catalyzed isomerization (observable in the pH range 5–7) shares a number of rate steps with acid dissociation (observable in the range from dilute acids to pH 4). The pH profile for the isomerization approaches as its upper limit the rate of dissociation in dilute acid. The latter is characterized by a single first-order process, $k_d = 0.38 \text{ s}^{-1}$,^{14,15} independent of pH over at least a limited range.¹⁵ This rate corresponds to the dissociation of the first Ni(II)–N bond, subsequent dissociations being rapid. If cis–trans isomerization involved only the dissociation of a single terminal N from the cis β form, followed by rapid ring closure to yield the trans isomer, the rate of isomerization would also be 0.38 s^{-1} , independent of pH. Thus, isomerization must involve dissociation of a secondary nitrogen as well. Also, either the cis complex must be cis α , requiring the dissociation of a second nitrogen in order to obtain the trans, or the complex is in the cis β configuration, but the secondary nitrogen must undergo inversion in order to coordinate the terminal nitrogen in the trans configuration.

Base-catalyzed isomerization of $\text{Ni}(2,3,2\text{-tet})(\text{H}_2\text{O})_2^{2+}$ may occur either by labilization of coordinated nitrogens by coordinated hydroxide (i.e., $\text{Ni}(2,3,2\text{-tet})(\text{H}_2\text{O})(\text{OH})^+$) or via the conjugate base mechanism postulated for base hydrolysis of, e.g., cobalt(III) complexes.¹⁶

In the mechanism shown in Figure 4, a number of rate constants are expected to have similar values; $k_1 \approx k_1'$, $k_2 \approx k_2'$, etc. From the mechanism and with these and a few other approximations, values for some of the rate and equilibrium constants shown can be estimated.

The rate law for cis to trans isomerization in neutral solution is

$$k_0 = \frac{K_1 k_2 k_{-2}'}{k_{-2} + k_{-2}'} \quad (10)$$

and, on the assumption that $k_{-2} = k_{-2}'$, $k_0 \approx K_1 k_2$. K_1 is the

equilibrium constant for the opening of a five-membered chelate ring. From the data of Paoletti et al.,¹⁷ $k_{-1}/k_1 \approx 10^5$. In combination with $k_0 = 1.1 \times 10^{-4} \text{ s}^{-1}$ and the acid dissociation rate, 0.38 s^{-1} ,^{14,15} the following rate constants are estimated: $k_1 = 0.38 \text{ s}^{-1}$, $k_{-1} = 4 \times 10^4 \text{ s}^{-1}$, $k_2 = 10 \text{ s}^{-1}$. The values of $4 \times 10^4 \text{ s}^{-1}$ for chelate ring closure and 10 s^{-1} for the opening of a six-membered chelate ring compare reasonably with values for other nickel(II) complexes.¹⁸

The rate of cis to trans isomerization in acid solution is

$$k_{\text{obsd}} = \frac{k_1 k_2^{\text{H}} K_1^{\text{H}} [\text{H}^+]}{k_{-1} + k_2^{\text{H}} K_1^{\text{H}} [\text{H}^+]} \quad (11)$$

which at high $[\text{H}^+]$ reduces to $k_{\text{obsd}} = k_1$. At lower acidities $k_{\text{obsd}} = K_1 k_2^{\text{H}} K_1^{\text{H}} [\text{H}^+]$, and thus $k_{\text{H}} = K_1 k_2^{\text{H}} K_1^{\text{H}} = 1900 \text{ M}^{-1} \text{ s}^{-1}$. With the approximation $k_2 \approx k_2^{\text{H}}$, then $K_1^{\text{H}} = k_{\text{H}}/k_0 = 10^{7.2}$, in agreement with the expected protonation constant of the terminal amino group.

Although the rates of formation and dissociation of metal complexes have been studied extensively, there are few instances in which rearrangements following initial coordination have been observed. The nickel(II) complex of 2,3,2-tet provides a convenient system for the observation of such a rearrangement, since there are large spectral differences between the octahedral and planar forms of the complex. We observe similar spectral changes upon mixing solutions of Ni^{2+} and the related ligand 3,2,3-tet, suggesting that rearrangement subsequent to coordination may occur relatively often. Certainly, the folded configuration is expected for coordination of macrocyclic tetraamines, and this is observed in the reaction of copper(II) with *teta* (*rac*-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane), where an unstable blue complex (*teta* in the folded configuration) is initially formed and slowly converts to a planar red complex.¹⁹ It is surprising that similar intermediates have not been reported in the formation of nickel(II) complexes of macrocyclic ligands.

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Registry No. *cis*-Ni(2,3,2-tet)(H_2O)₂²⁺, 74867-36-0; *trans*-Ni(2,3,2-tet)(H_2O)₂²⁺, 23236-28-4; Ni(2,3,2-tet)²⁺, 25669-75-4.

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