has increased, is consistent with the observation that separation of carboxyl oxygen atoms, in general, is insufficient to allow both atoms to coordinate directly with a single metal cation in lieu of water molecules.

The value of $f(\mu)$ at $\mu = 0.1$ (the activity correction to the $K_1/K_2$ ratio in this case) is estimated to be about 0.67, assuming that

$$\log \gamma_i = -0.509Z_i^2\{\sqrt{\mu}/(1 + 2\sqrt{\mu}) - 0.2\mu\}$$

This assumption yields $RT = 1.83$, setting a practical upper limit of 1.83 on the coulombic factor $T$, since it is difficult to imagine an $R$ factor ever less than unity because steric and asymmetry factors tend to attenuate affinity of the acceptor for subsequent ligands. Following this line of argument, previous data of Powell and Rowlands (average $K_1/K_2 = 4.93$ for elements La–Nd and 3.29 for elements Tb–Lu) establish an even smaller upper limit of 1.5 on the coulombic factor for the case of lanthanide associations with 1-hydroxycyclopentanecarboxylate, an analogous ligand. The present findings and those of Powell and Rowlands could be correlated rather simply by assuming that $T = 1.5$, as Manning has proposed.[4] For this assumption to be valid it would be necessary that the rest factor $R$ (primarily steric in origin) be unity in the case of small "tied together" alkyl groups as in 1-hydroxycyclopentanecarboxylate, but greater when the alkyl substituents of the $\alpha$-hydroxycarboxylate entity are bulky and/or free to cause local disturbances by rotating. In the present case, $R$ would then be 1.22, because the ethyl radical is not linear and can rotate about its attachment to the $\alpha$-carbon atom. While the smaller ratios of Powell and Rowlands strongly suggest that $T$ does not exceed a value of 1.5 in these systems, the possibility that the coulombic factor is actually somewhat less than this maximum figure cannot be ruled out. Consequently, it may be that $R$ actually exceeds unity in the case of HCPC and is correspondingly greater than 1.22 in the case of the HMBA anion. Certainly it appears safe to assume that $1.0 < T < 1.5$ for the process $Ln^{3+} \rightarrow LnL^{2+} \rightarrow LnL_2^+$, that $1.0 < R < 1.5$ in the case of HCPC, and that $1.22 < R < 1.83$ with HMBA.

---

CONTRIBUTION NO. 1721 FROM THE DEPARTMENT OF CHEMISTRY,
INDIANA UNIVERSITY, BLOOMINGTON, INDIANA 47401

# Hindered Ligand Systems. III. Kinetics of the Dissociation of the Nickel(II) Complex of *cis,cis*-1,3,5-Triaminocyclohexane

BY R. F. CHILDERS AND R. A. D. WENTWORTH

*Received April 30, 1969*

The bis complexes of *cis,cis*-1,3,5-triaminocyclohexane, $M(cis,cis\text{-tach})_2^{2+}$ (M = Co, Ni, Zn, Cd), were recently prepared and characterized.[1] As with the bis complexes[2] of Co(III) and Rh(III), all available evidence indicated that the ligands are bonded to the trigonal faces of an octahedron. In addition, it was found that in the case of Ni(II) only, it was possible to prepare and isolate the mono complex according to

$$Ni(cis,cis\text{-tach})_2^{2+} + Ni^{2+} \longrightarrow 2Ni(cis,cis\text{-tach})^{2+} \qquad (1)$$

(with waters of hydration omitted). Subsequent studies of this new species led to the discovery of its extraordinary kinetic stability in the presence of mineral acids. The half-life of the reaction

$$Ni(cis,cis\text{-tach})^{2+} + 3H^+ \longrightarrow Ni^{2+} + cis,cis\text{-tach}H_3^{3+} \qquad (2)$$

in 5 $M$ $HNO_3$ is about 7 min at 25°. In contrast, the dissociation of $Ni(dien)^{2+}$ [3] in solutions of the same acidity is nearly instantaneously complete.

A more detailed study of the dissociation of $Ni(cis,cis\text{-tach})^{2+}$ in 0.5–5 $M$ $HNO_3$ has now been completed and the results are reported herein.

## Experimental Section

**$Ni(cis,cis\text{-tach})(NO_3)_2 \cdot 3H_2O$.**—The preparation of this compound was previously described.[1] However, eq 1 tends to be reversed in hot alcohol, which is the prescribed solvent for recrystallization, and the desired product is inevitably contaminated with small quantities of the bis complex. This occurrence was prevented by recrystallizing the mono complex from 95% alcohol containing excess $Ni(NO_3)_2 \cdot 6H_2O$. Generally, large prismatic crystals of the desired compound were obtained from the slow evaporation of saturated solutions. The complex could be obtained more rapidly by removing the solvent with a rotary evaporator. This technique provided poorly formed crystals which, however, were quite satisfactory for kinetic purposes. In either case the crystals were washed with a small quantity of water, followed by alcohol and then ether.

The spectrum of this compound in aqueous solution (with the ionic strength adjusted to 1.00 with $NaNO_3$) consists of bands at 361 ($\epsilon$ 11.2), 588 ($\epsilon$ 9.2), and 969 m$\mu$ ($\epsilon$ 8.8).

**Kinetic Measurements.**—The initial studies were conducted in $HNO_3$ solutions with $[H^+] \geqslant 1$ $M$. In each run a precisely weighed quantity of the complex was dissolved in about 3 ml of $H_2O$, followed by addition of 5–15 $M$ $HNO_3$. Later studies were conducted at $[H^+] < 1$ $M$ in solutions whose ionic strength was adjusted to 1.00 with $NaNO_3$. These solutions were prepared by dissolving a precisely weighed quantity of the complex in a thermostated stock solution which contained the desired quantities of $HNO_3$ and $NaNO_3$. All samples were then well mixed and transferred to a thermostated sample cell in the spectrophotometer. The "zero time" spectrum was then recorded (approximately 4 min after dilution).

In the absence of any bis complex, isosbestic points were observed at 385 ± 1 ($\epsilon$ 4.9), 468 ± 1 ($\epsilon$ 0.33), and 686 ± 2 m$\mu$ ($\epsilon$ 1.8) throughout a kinetic run. If the compound had not been recrystallized in the presence of excess $Ni(NO_3)_2 \cdot 6H_2O$, true isosbestic points did not exist through the early stages of a reaction. Using the absorbancy at 575 m$\mu$, the pseudo-first-order rate constant was derived from the equation $\ln [(A_t - A_\infty)/(A_0 - A_\infty)] = -k_{obsd}t$. In the initial studies of the dissociation at $[H^+]$ between 1 and 5 $M$, rate plots generally showed a slight curvature through about the first 25–50% of the reaction but were then linear to at least 94% completion. The major portion of the curvature was traced to local heating caused by dilution of relatively concentrated acid solutions. An additional cause was traced to the method of recrystallization since the crystals used in these runs were not recrystallized from solu-

---

[1] R. A. D. Wentworth, *Inorg. Chem.*, **7**, 1030 (1968).

[2] R. A. D. Wentworth and J. J. Felten, *J. Am. Chem. Soc.*, **90**, 621 (1968).

[3] In this paper the following abbreviations have been used: dien, bis(2-aminoethyl)amine (diethylenetriamine); dapa, bis(3-aminopropyl)amine· ptn, 1,2,3-propanetriamine.

tions containing $Ni(NO_3)_2 \cdot 6H_2O$. For $[H^+] < 1$ *M* and $\mu = 1.00$, recrystallization was accomplished in this manner and pseudo-first-order rate constants were obtained from the initial slopes of the rate plots which were linear for only about 0.8–1.5 half-lives after temperature equilibrium due to depletion of the available acid.

**Instrumentation.**—The visible spectra were recorded using a Cary Model 14 spectrophotometer with matched quartz cells. The sample cell was held in a thermostated cell block. The solution temperature in the sample cell was monitored with a copper–constantan thermocouple in conjunction with a Leeds and Northrup potentiometer.

## Results and Discussion

The results of a study of the dissociation of Ni(*cis*,*cis*-tach)$^{2+}$ according to eq 2 with $[H^+]$ between 1 and 5 *M* are given in Table I. Although there was no attempt to control the ionic strength, these results suggest that the rate equation can be expressed as

$$-\frac{d \ln [\text{complex}]}{dt} = k_{obsd}$$

with $k_{obsd} = k + k_H[H^+]$. There was no indication that further increases in the acid concentration would eventually bring about an observed rate constant which was independent of $[H^+]$. Subsequent studies were then conducted at acid concentrations between 0.5 and 0.8 *M* with the ionic strength adjusted to 1.00 with $NaNO_3$. The results at 25, 35, and 45° are given in Table I, are shown in Figure 1, and substantiate the rate equation. The values of $k$ and $k_H$, as well as the activation parameters, are given in Table II.

TABLE I
FIRST-ORDER RATE CONSTANTS FOR THE DISSOCIATION OF Ni(*cis*,*cis*-tach)$^{2+}$ IN AQUEOUS NITRIC ACID[a]

| Temp, °C[b] | [Complex]$_0$, *M* | $[HNO_3]_0$, *M* | $10^4 k_{obsd}$, $sec^{-1}$ |
|---|---|---|---|
| 25.00 | 0.060 | 1.00 | 3.80[c–e] |
| 25.00 | 0.0730 | 1.99 | 5.95[c–e] |
| 25.00 | 0.0537 | 2.98 | 10.1[c–e] |
| 25.00 | 0.0658 | 4.95 | 16.6[c–e] |
| 25.00 | 0.0670 | 0.804 | 2.40 |
| 25.00 | 0.0668 | 0.708 | 2.34 |
| 25.00 | 0.0454 | 0.615 | 2.12 |
| 25.00 | 0.0700 | 0.596 | 1.90[d,e] |
| 25.00 | 0.0414 | 0.598 | 1.98[d,e] |
| 25.00 | 0.0671 | 0.520 | 2.03 |
| 34.73 | 0.0668 | 0.793 | 7.30 |
| 34.73 | 0.0684 | 0.697 | 6.92 |
| 34.73 | 0.0685 | 0.594 | 6.29 |
| 34.73 | 0.0684 | 0.497 | 5.84 |
| 34.73 | 0.0678 | 0.447 | 5.61 |
| 44.42 | 0.0667 | 0.795 | 21.1 |
| 44.42 | 0.0670 | 0.697 | 19.7 |
| 44.42 | 0.0669 | 0.595 | 17.7 |
| 44.42 | 0.0664 | 0.496 | 17.0 |

[a] The ionic strength, which was controlled with $NaNO_3$, was adjusted to 1.00 in all cases, except where noted. [b] The estimated maximum deviation in the temperatures is ±0.08°. [c] No $NaNO_3$ added. [d] Contaminated with small quantities of the bis complex. [e] Not used to obtain resolved rate constants.

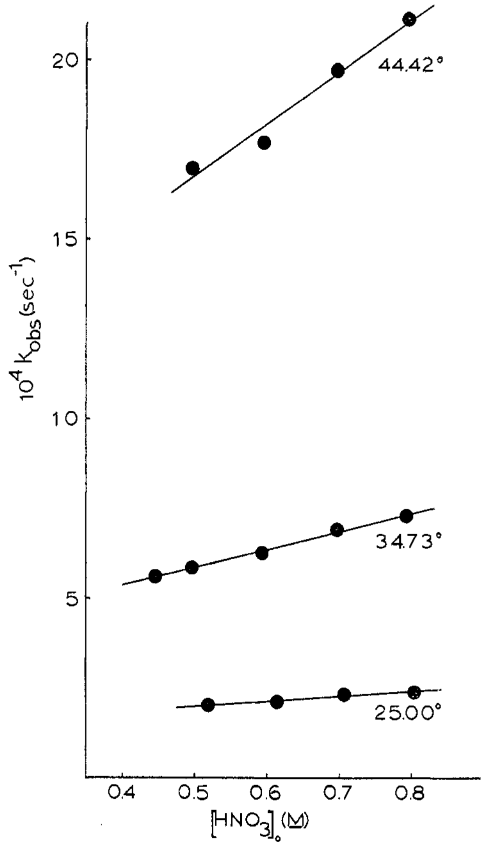
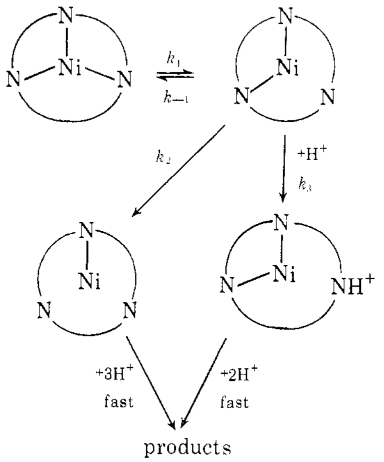


Figure 1.—The variation of $k_{obsd}$ with the initial acidity at 25.00, 34.73, and 44.42°.

In contrast to these results the dissociative rates of Ni(dien)$^{2+}$, Ni(dapa)$^{2+}$, and Ni(ptn)$^{2+}$ are much greater and become completely independent of $[H^+]$ at acid concentrations greater than 0.2 *M* at the same ionic strength.[4] The activation parameters associated with each reaction are nearly identical and point to a common mechanism. A generally accepted mechanism for the dissociation of chelate compounds, which has been given by Basolo and Pearson,[5] will readily explain the observed rate equations for these dissociations.

We assume that the dissociation of Ni(*cis*,*cis*-tach)$^{2+}$ can be explained in terms of a similar mechanism, which appears schematically as



If it is assumed that $k_{-1} >> k_2 + k_3[H^+]$, the rate equation becomes

---

[4] G. A. Melson and R. G. Wilkins, *J. Chem. Soc.*, 2662 (1963).
[5] F. Basolo and R. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, John Wiley & Sons, Inc., New York, N. Y., 1967, p 216.

$$-\frac{d \ln [\text{complex}]}{dt} = K(k_2 + k_3[\text{H}^+])$$

with $K = k_1/k_{-1}$. The observed rate equation has this form.

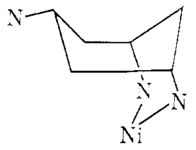
The actual stereochemistry of the intermediate containing two Ni–N bonds is important in assessing the credibility of the assumption upon which the rate law is based. Breakage of the first Ni–N bond necessarily forces one of the remaining six-membered rings into an unstable boat conformation. The conformational change in **1** was achieved by rotation within the cyclohexane ring across a potential barrier which should be about 10 kcal mol$^{-1}$ by analogy with other cyclohexanes.[6] The triaxial conformation of the cyclohexane ring is retained in **2**, but a conformational change has occurred within the metal-containing ring. The potential barrier for this process is unknown. We cannot, therefore, easily rule out either **1** or **2** on the basis of energetics, and it is possible that they both play a role in the dissociative process. Nevertheless, both **1** and **2** contain nonbonded contacts which will cause either of them to be highly unstable. These repulsive forces are best relieved by returning to the tridentate form of the ligand, and re-forming the Ni–N bond should be a very favorable process. The assumption which was used in obtaining the rate equation at least seems plausible due to this reason, and, in addition, the less-than-normal ability[4] of the acid to scavenge the partially dissociated ligands is explicable now.

TABLE II

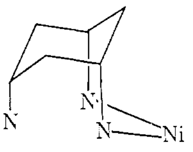
RATE CONSTANTS AND ACTIVATION PARAMETERS

| Temp, °C | $10^4k$, sec$^{-1}$ | $10^4k_H$, $M^{-1}$ sec$^{-1}$ |
|---|---|---|
| 25.00 | 1.30 | 1.39 |
| 34.73 | 3.35 | 5.02 |
| 44.42 | 9.53 | 14.5 |
| $E_a$, kcal mole$^{-1}$ [a] | 19.3 ± 0.9 | 22.7 ± 0.8 |
| $\Delta S^{\ddagger}$, cal deg$^{-1}$ mol$^{-1}$ | −13.5 ± 3.1 | −2.0 ± 2.8 |

[a] Errors are standard deviations obtained by the method of least squares.



1



2

**Acknowledgment.**—Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

---

[6] E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p 205.

---

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
KANSAS STATE UNIVERSITY, MANHATTAN, KANSAS 66502

## Preparation-Controlled Forms of Copper(II) and Nickel(II) Ethylenediaminetetraacetato Complex Diprotic Acids

BY CHARLES L. FOXX AND JACK L. LAMBERT

*Received June 5, 1969*

Dihydrogen ethylenediaminetetraacetatoaquocopper(II), $\text{CuYH}_2\cdot\text{H}_2\text{O}$, has been studied by several groups of investigators, but several discrepancies persist regarding its structure and properties. We have evidence that two forms exist, a monohydrate and an anhydrous species, depending upon the method of preparation. Slow crystallization by evaporation at 40° in a vacuum oven produces the dark blue monohydrate. Rapid crystallization from solution supersaturated at boiling temperature or by addition to excess ethanol produces the anhydrous compound. The analogous nickel(II) compounds are formed by similar treatments, and preliminary work indicates two forms also for zinc and cobalt(II). Manganese(II) appears to have only one form.

Brintzinger and Hesse[1] prepared a greenish blue copper(II) EDTA compound that was shown by analysis to be the anhydrous $\text{CuYH}_2$. This compound did not lose weight until decomposition set in above 200°. They concluded that the structure was the square-planar complex. Kirschner[2] prepared the monohydrate, $\text{CuYH}_2\cdot\text{H}_2\text{O}$, in which he proposed quadridentate complexation by the ligand because of the equal intensities of the antisymmetric stretching frequencies of the coordinated carboxylate groups and the uncoordinated carboxylic acid groups. Smith and Hoard[3] and Garvan[4] examined $\text{CuYH}_2\cdot\text{H}_2\text{O}$ by X-ray diffraction and infrared spectroscopy. Both found the copper(II) compound to be isomorphous with $\text{NiYH}_2\cdot\text{H}_2\text{O}$ and concluded that the ligand is quinquedentate and the structure octahedral. Bhat and Iyer[5] prepared a compound that analysis indicated to be the monohydrate but which showed no weight loss until melting followed by decomposition above 238°. Martynenko, *et al.*,[6,7] studied the copper(II)–EDTA system and concluded that there are no less than four species, including the monohydrate, an unstable anhydrous form, a stable anhydrous form, and a dehydrated form. The monohydrate was crystallized from solutions of the complex acid less that 0.1 $M$, and the

---

(1) H. Brintzinger and G. Hesse, *Z. Anorg. Allgem. Chem.*, **249**, 113 (1942).

(2) S. Kirschner, *J. Am. Chem. Soc.*, **78**, 2372 (1956).

(3) G. S. Smith and J. L. Hoard, *ibid.*, **81**, 556 (1959).

(4) F. L. Garvan, Ph.D. Thesis, University of Sydney, Sydney, Australia (from F. L. Garvan, "Chelating Agents and Metal Chelates," F. P. Dwyer and D. P. Mellor, Ed., Academic Press, New York, N. Y., 1964, p 297).

(5) T. R. Bhat and R. K. Iyer, *J. Inorg. Nucl. Chem.*, **29**, 179 (1967).

(6) L. I. Martynenko, N. I. Pechurova, E. N. Efremov, and A. I. Grigorev, *Zh. Neorgan. Khim.*, **12**, 424 (1967).

(7) L. I. Martynenko, N. I. Pechurova, and N. P. Potapova, *ibid.*, **13**, 2067 (1968).