Formation and Dissociation Kinetics and Crystal Structures of Nickel(II)−Macrocyclic Tetrathiaether Complexes in Acetonitrile. Comparison to Nickel(II)−Macrocyclic Tetramines

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Complex formation and dissociation rate constants have been independently determined for solvated nickel(II) ion reacting with eight macrocyclic tetrathiaether ligands and one acyclic analogue in acetonitrile at 25 °C, $\mu =$ 0.15 M. The macrocyclic ligands include 1,4,8,11-tetrathiacyclotetradecane ([14]aneS_4) and seven derivatives in which one or both ethylene bridges have been substituted by *cis*- or *trans*-1,2-cyclohexane, while the acyclic ligand is 2,5,9,12-tetrathiatridecane (Me_2-2,3,2-S_4). In contrast to similar complex formation kinetic studies on Ni(II) reacting with corresponding macrocyclic tetramines in acetonitrile and *N*,*N*-dimethylformamide (DMF), the kinetics of complex formation with the macrocyclic tetrathiaethers show no evidence of slow conformational changes following the initial coordination process. The differing behavior is ascribed to the fact that such conformational changes require donor atom inversion, which is readily accommodated by thiaether sulfurs but requires abstraction of a hydrogen from a nitrogen (to form a temporary amide). The latter process is not facilitated in solvents of low protophilicity. The rate-determining step in the formation reactions appears to be at the point of first-bond formation for the acyclic tetrathiaether but shifts to the point of chelate ring closure (i.e., second-bond formation) for the macrocyclic tetrathiaether complexes. The formation rate constants for Ni(II) with the macrocyclic tetrathiaethers parallel those previously obtained for Cu(II) reacting with the same ligands in 80% methanol−20% water (w/w). By contrast, the Ni(II) dissociation rate constants show significant variations from the trends in the Cu(II) behavior. Crystal structures are reported for the Ni(II) complexes formed with all five dicyclohexanediyl-substituted macrocyclic tetrathiaethers. All but one are low-spin species.

Introduction

Complex formation reactions between many divalent solvated transition metal ions and a variety of *unidentate* and *acyclic multidentate* ligands have been correlated to the rate of inner-sphere solvent exchange on the metal ion in terms of the Eigen−Wilkins mechanism.[2,3] Attempts to interpret complexation rate constants with *macrocyclic* ligands in the same manner have been relatively unsuccessful as noted in a recent review by Elias[4] in which the major focus was on macrocyclic tetramines.[5] In the current study, we examine the mechanistic implications of complex formation and dissociation kinetics of solvated nickel(II) reacting with a series of macrocyclic tetrathiaethers in acetonitrile and compare these to the macrocyclic tetramines.

In aqueous solution, metal complexation kinetic studies have primarily been conducted at pH < 7 to avoid metal hydroxide precipitation. Under these conditions, macrocyclic tetramines exist as a mixture of protonated species. In an early kinetic study, Kaden[6] reported that both the mono- and diprotonated species of cyclam (1,4,8,11-tetraazacyclotetradecane) react 30 000 times more slowly with aquated Ni(II) than do corresponding acyclic species.[7] That this difference is primarily attributable to enhanced intramolecular H-bonding in macrocyclic tetramines was suggested by subsequent kinetic studies conducted in our laboratory at pH ≥ 13 in which $Cu(OH)_3^-$ was shown to exhibit nearly identical complex formation rate constants when reacted with *unprotonated* acyclic and macrocyclic polyamines.[8] Since no data are available for solvent exchange on $Cu(OH)_3^-$, however, formation rate constants with this metal species cannot be interpreted in terms of the discrete mechanistic steps prescribed by the Eigen−Wilkins mechanism.

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(5) Studies involving crown ethers have focused on their reaction kinetics with alkali metal ions for which the kinetic parameters for the dissociation of single metal−solvent bonds cannot be characterized because of their lability. Instead, the overall complexation kinetics are largely controlled by ligand conformational changes (the Eigen−Winkler mechanism). (a) Diebler, H.; Eigen, M.; Ilgenfritz, G.; Maass, G.; Winkler, R. *Pure Appl. Chem.* **1969**, *20*, 93−115. (b) Eigen, M. In *Quantum Statistical Mechanics in the Natural Sciences*; Kursunoglu, B., Mintz, S. L., Widmayer, S. M., Eds.; Plenum: New York, 1974; pp 37−61. (c) Chock, P. B.; Eggers, F.; Eigen, M.; Winkler, R. *Biophys. Chem.* **1977**, *6*, 239−251.

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As an alternative approach for circumventing ligand protonation, Hay and Norman,[9] Hertli and Kaden,[10] and Elias and coworkers[11−13] studied the kinetics of macrocyclic tetramines reacting with solvated Ni(II) in aprotic solvents—specifically, acetonitrile, *N,N*-dimethylformamide (DMF), and dimethyl sulfoxide (DMSO). Their results showed evidence of two or three discrete reaction processes. Although the initial second-order process is presumed to represent either first- or second-bond formation, no correlation was established with the rate constants for inner-sphere solvent exchange.[4]

As we have noted in earlier work,[14] polythiaethers are insensitive to pH and yet still form complexes of measurable stability with Cu(II) in aqueous solution. Because of the limitations of their aqueous solubility, however, formation kinetic studies on Cu(II)−macrocyclic polythiaethers have been conducted primarily in methanol−water mixtures where the rate constants for inner-sphere solvent exchange are unknown. No evidence for multiple reaction steps have been observed. Extrapolation to aqueous conditions[14] and subsequent aqueous studies of water-soluble polythiaethers[15,16] have indicated that ring closure is the rate-determining step.

We now report the first measurements on the kinetics of solvated Ni(II) reacting with a series of eight macrocyclic tetrathiaethers and an acyclic analogue (Figure 1). Acetonitrile has been utilized as the solvent to solubilize the ligands and enhance complex formation. Dissociation rate constants for the Ni(II) complexes have been determined independently by utilizing Cu(II) as a scavenger for the ligand. The ratios of the formation and dissociation rate constants are compared with recently determined stability constants[17] to establish whether there is evidence for the buildup of reaction intermediates as indicated in the corresponding macrocyclic tetramine studies in nonaqueous solvents.[11−12] Since the rate constant for inner-sphere solvent exchange with bulk solvent is known for $Ni(CH_3CN)_6^{2+}$,[18,19] the applicability of the Eigen−Wilkins mechanism can be tested directly for these reactions. Moreover, the results provide the first direct comparison between the kinetic reactivity of macrocyclic polythiaethers and polyamines with the same metal ion (Ni(II)) in the same solvent medium (acetonitrile).

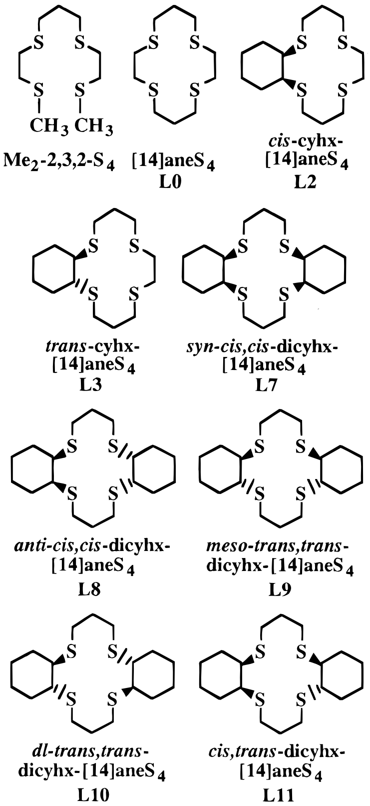

Figure 1. Ligands included in this work. Numbers assigned to the ligands correspond to designations used in earlier work (refs 17, 22, 30).

Crystallographic structures for the Ni(II) complexes with all eight macrocyclic tetrathiaether ligands have also been determined,[20,21] five being newly determined in this work. These are compared to the structures for the related macrocyclic tetramine complexes.

Experimental Section

Reagents. The syntheses of the seven cyclohexanediyl derivatives of [14]aneS_4 (Figure 1) have been described previously.[22] The $Ni(ClO_4)_2$, $Cu(ClO_4)_2$, and $NaClO_4$ salts used for the current studies were prepared by the slow addition of $HClO_4$ to the corresponding nickel, copper, and sodium carbonates, respectively. The products were first recrystallized as hydrated salts from water and then recrystallized from acetonitrile by evaporation to yield the acetonitrile-solvated salts. [WARNING! *Metal perchlorate salts are potentially explosive; the isolated salts should never be dried and should not be subjected to shock!! When recrystallizing from acetonitrile, metal perchlorate solutions should never be heated but should be allowed to evaporate at room temperature, and only small quantities should be prepared with suitable protective measures.*] HPLC grade acetonitrile was obtained from Fisher Scientific. A previous Karl Fischer determination revealed that the water content was 0.017% (w/w) in a bottle of solvent that had been opened 3 weeks earlier.[23] In the current kinetic studies, the addition of up to 1% water was found to have no effect upon the

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Table 1. Maximum Absorbance Peaks, Formation and Dissociation Rate Constants, and Stability Constants for Nickel(II)−Tetrathiaether Complexes in Acetonitrile at 25 °C, $\mu = 0.15$ M (Except As Noted) ($NaClO_4$)

complexed ligand	λ_{max}, nm {$10^{-3}\epsilon$, M^{-1} cm^{-1}}	k_f,[a] M^{-1} s^{-1}	10^2k_d,[a,b] s^{-1}	$10^{-4}k_f/k_d$, M^{-1}	$10^{-4}K_{Ni^{II}L}$,[a,c] M^{-1}
Me_2-2,3,2-S_4	312 {17(1)}	72(1)			
[14]aneS_4 (**L0**)	302 {3.3(3)}	3.9(1)	12.0(4),[d] 17(7)[e]	0.0033, 0.0023	0.0036(3)
cis-cyhx-[14]aneS4 (**L2**)	310 {4.08(5)}	3.4(5)	0.67(2)[f]	0.051	0.075(3)
trans-cyhx-[14]aneS_4 (**L3**)	306 {12.2(5)}	2.8(4)	0.33(1)[g]	0.088	0.20(1)
syn-cis,cis-dicyhx-[14]aneS_4 (**L7**)	314 {27.5(9)}	10.1(6)	0.0072(2)	14	13.6(4)
anti-cis,cis-dicyhx-[14]aneS_4 (**L8**)	310 {14.7(7)}	2.6(1)	0.00762(0)	3.5	3.4(2)
meso-trans,trans-dicyhx-[14]aneS_4 (**L9**)	308 {22.5(6)}	6.5(6)	0.00116(3)	56	44(3)
dl-trans,trans-dicyhx-[14]aneS_4 (**L10**)	308 {10.5(1)}	5.0(2)	0.0014(3)	38	36(7)
cis,trans-dicyhx-[14]aneS_4 (**L11**)	310 {9.81(3)}	5.7(5)	0.057(2)	10	9.2(3)

[a] Values in parentheses are standard deviations in terms of the last digit shown; thus, 72(1) and 0.120(4) represent 72 ± 1 and 0.120 ± 0.004, respectively. [b] Obtained from Cu(II) displacement kinetics except as noted. [c] Stability constant data from ref 17. [d] Intercept from a plot of eq 3. [e] Total $Ni(ClO_4)_2$ concentration was 1.0 M; $\mu = 3.0$ M. [f] Total $Ni(ClO_4)_2$ concentration was 0.10 M; $\mu = 0.45$ M. [g] Total $Ni(ClO_4)_2$ concentration was 0.040 M; $\mu = 0.27$ M.

Table 2. Crystal Parameters and Experimental Data for X-ray Diffraction Measurements on the Perchlorate Salts of Nickel(II) Complexes with the Dicyclohexanediyl Derivatives of [14]aneS_4

parameter	$[Ni^{II}(\mathbf{L7})](ClO_4)_2$	$[Ni^{II}(\mathbf{L8})](ClO_4)_2$	$[Ni^{II}(\mathbf{L9})](ClO_4)_2$	$[Ni^{II}(\mathbf{L10})](ClO_4)_2$	$[Ni^{II}(\mathbf{L11})(CH_3CN)_2](ClO_4)_2$
empirical formula	$NiC_{18}H_{32}S_4Cl_2O_8$	$NiC_{18}H_{32}S_4Cl_2O_8$	$NiC_{18}H_{32}S_4Cl_2O_8$	$NiC_{18}H_{32}S_4Cl_2O_8$	$NiC_{22}H_{38}S_4N_2Cl_2O_8$
fw	634.29	634.29	634.29	634.29	716.39
space group	$P2_12_12_1$	$P\bar{1}$	$C2/c$	$P2_12_12_1$	$P2_1$
a, Å	12.3856(6)	7.3849(6)	17.738(1)	9.5786(6)	9.603(2)
b, Å	12.8029(7)	8.8365(7)	7.0613(4)	14.1790(7)	14.304(3)
c, Å	16.4921(9)	9.7503(8)	20.971(1)	19.081(1)	11.774(2)
α, deg	90	83.428(2)	90	90	90
β, deg	90	76.639(1)	99.699(1)	90	105.48(3)
γ, deg	90	87.677(1)	90	90	90
V, Å^3	2615.2(2)	614.92(9)	2589.1(3)	2591.5(2)	1558.6(5)
Z	4	1	4	4	2
ρ_{calcd}, g cm^{-3}	1.611	1.713	1.627	1.626	1.526
μ, mm^{-1}	1.306	1.389	1.320	1.318	1.107
$R(F)$[b]	0.0476	0.0421	0.0623	0.0554	0.0618
$R_w(F^2)$[c]	0.1132	0.0773	0.1517	0.1313	0.1627

[a] $T = 295(2)$ K; $\lambda = 0.717\,03$ Å. [b] $R(F) = |F_c||/\sum|F_o|$ for $2\sigma(I)$ reflections. [c] $R_w(F^2) = [\sum(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$ for $2\sigma(I)$ reflections.

observed reaction kinetics. This is consistent with earlier observations by Chattopadhyay and Coetzee[24] on Ni(II) complex formation kinetics in acetonitrile. Therefore, no attempt was made to dry the solvent further.

Acetonitrile solutions of $Ni(ClO_4)_2$ and $Cu(ClO_4)_2$ were standardized by dilution with water followed by titration with a standard EDTA solution using murexide indicator. Ligand solutions were standardized spectrophotometrically by mole-ratio plots against standard Cu(II).

Kinetic Measurements. All kinetic measurements were monitored spectrophotometrically using the maximum absorption peaks and molar absorptivity values previously determined (Table 1).[17] A Cary model 17D dual-beam recording spectrophotometer was used for the spectrophotometric mole-ratio plots and for the kinetics of nearly all dissociation reactions. The kinetic measurements for all complex formation reactions and the most rapid dissociation reaction were made using a Durrum D-110 stopped−flow spectrophotometer equipped with a modified flow system, designed and built by Tritech Scientific Ltd. of Winnipeg, Manitoba, Canada. This flow system contained all Teflon gaskets, thereby avoiding the leakage problems inherent when using acetonitrile in the original rubber gasket system. The instrument was interfaced to an Insight 486 PC for data collection and analysis using software developed in-house. For kinetic measurements involving both the Cary and Durrum spectrophotometers, the temperature was maintained at 25.0 ± 0.2 °C using a circulating temperature bath. For all measurements, the ionic strength was maintained at 0.15 M using $NaClO_4$ except as otherwise noted.

Crystal Structures. Crystals of the Ni(II) complexes formed with the five dicyclohexanediyl derivatives of 1,4,8,11-tetrathiacyclotetradecane (**L7**−**L11** in Figure 1) were grown by slow evaporation from acetonitrile containing stoichiometric amounts of $Ni(ClO_4)_2$ and ligand. Diffraction data were collected on a Siemens/Bruker P4/CCD diffractometer equipped with monochromated Mo Kα radiation and the manufacturer's SMART collection software and SAINT processing software. A hemisphere of data were collected at 10 s/frame with 0.3° between each frame. Absorption corrections were applied with the program SADABS.[25] The structure was solved and refined on F^2 with the programs SHELXS and SHELXL-93.[25] Hydrogen atoms were placed in calculated or observed positions. All non-hydrogen atoms were anisotropically described except some isotropically refined partial atoms in disordered perchlorate groups. The experimental parameters for all five structures are presented in Table 2.

Results

Structural Determinations. The crystal structures for the Ni(II) complexes with [14]aneS_4 (**L0**)[20] and the two monocyclohexanediyl derivatives (**L2** and **L3**)[21] have been previously reported in the literature. The crystal structures of the Ni(II) complexes with the five dicyclohexanediyl derivatives were resolved as part of the current investigation. The bond lengths and bond angles of primary interest are compiled in Table 3. (For those structures involving higher symmetry, some bond distances and angles are repeated to facilitate comparison.) As illustrated by the ORTEP drawings in Figures 2−6, four of the five Ni(II) complexes are square-planar and, therefore, have low spin. The Ni^{II}(**L11**) complex crystallized with two axially coordinated acetonitrile ligands to generate a high-spin six-coordinate complex.

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Table 3. Average Crystallographic Bond Lengths and Bond Angles in the Cationic Units of the Perchlorate Salts of Nickel(II) Complexes with the Dicyclohexanediyl Derivatives of [14]aneS_4

Bond Length, Å

	$[Ni^{II}(\mathbf{L7})](ClO_4)_2$	$[Ni^{II}(\mathbf{L8})](ClO_4)_2{}^a$	$[Ni^{II}(\mathbf{L9})](ClO_4)_2$	$[Ni^{II}(\mathbf{L10})](ClO_4)_2{}^b$	$[Ni^{II}(\mathbf{L11})](CH_3CN)_2(ClO_4)_2{}^c$
Ni−S(1)	2.195(1)	2.1830(5)	2.1792(9)	2.194(2)	2.332(2)
Ni−S(2)	2.182(1)	2.1882(5)	2.1792(9)	2.191(2)	2.334(2)
Ni−S(3)	2.179(1)	2.1830(5)	2.1827(9)	2.186(2)	2.321(2)
Ni−S(4)	2.200(1)	2.1882(5)	2.1827(9)	2.185(2)	2.317(2)
Ni−N(1) (or Ni−O)		(3.052)		(2.932)	2.178(8)
Ni−N(2) (or Ni−O)		(3.052)		(3.190)	2.134(7)

Bond Angle, deg

	$[Ni^{II}(\mathbf{L7})](ClO_4)_2$	$[Ni^{II}(\mathbf{L8})](ClO_4)_2{}^a$	$[Ni^{II}(\mathbf{L9})](ClO_4)_2$	$[Ni^{II}(\mathbf{L10})](ClO_4)_2{}^b$	$[Ni^{II}(\mathbf{L11})](CH_3CN)_2(ClO_4)_2{}^c$
S(1)−Ni−S(2)	89.31(5)	89.74(2)	90.20(4)	91.27(6)	89.15(6)
S(2)−Ni−S(3)	94.64(5)	90.26(2)	89.81(4)	89.61(6)	88.68(7)
S(3)−Ni−S(4)	89.50(5)	89.74(2)	90.20(4)	90.70(6)	89.61(7)
S(4)−Ni−S(1)	86.51(5)	90.26(2)	89.81(4)	89.30(6)	92.52(7)
S(1)−Ni−S(3)	175.63(5)	180.0	180.0	174.35(6)	177.56(7)
S(2)−Ni−S(4)	175.66(66)	180.0	180.0	171.13(6)	177.30(8)

Ni Displacement from Mean S_4 Plane (Å)

$[Ni^{II}(\mathbf{L7})](ClO_4)_2$	$[Ni^{II}(\mathbf{L8})](ClO_4)_2{}^a$	$[Ni^{II}(\mathbf{L9})](ClO_4)_2$	$[Ni^{II}(\mathbf{L10})](ClO_4)_2{}^b$	$[Ni^{II}(\mathbf{L11})](CH_3CN)_2(ClO_4)_2{}^c$
0	0.031	0	0.029	0.033

[a] Bond angles (deg) to apical (nonbonded) perchlorate oxygens in Ni(**L8**) are the following: S(1)−Ni−O(4), 93.4; S(2)−Ni−O(4), 88.0. [b] Bond angles (deg) to apical (nonbonded) perchlorate oxygens in Ni(**L10**): S(1)−Ni−O(2), 75.9; S(1)−Ni−O(1a), 86.1; S(2)−Ni−O(2), 74.3; S(2)−Ni−O(1a), 94.6; S(3)−Ni−O(2), 109.7; S(3)−Ni−O(1a), 88.3; S(4)−Ni−O(2), 97.3; S(4)−Ni−O(1a), 94.3; O(2)−Ni−O(1a), 158.3. [c] Bond angles (deg) to apical nitrogens in Ni^{II}(**L11**): S(1)−Ni−N(1), 93.9(2); S(1)−Ni−N(2), 85.3(2); S(2)−Ni−N(1), 85.3(2); S(2)−Ni−N(2), 93.6(2); S(3)−Ni−N(1), 84.8(2); S(3)−Ni−N(2), 95.9(2); S(4)−Ni−N(1), 92.5(2); S(4)−Ni−N(2), 88.6(2); N(1)−Ni−N(2), 178.6(3).

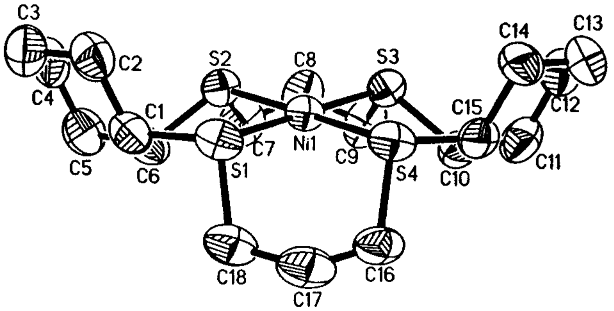

Figure 2. ORTEP drawing showing the structure of the cationic unit for $[Ni^{II}$(*syn-cis,cis*-dicyhx-[14]aneS_4)]$(ClO_4)_2$ (i.e., Ni^{II}(**L7**)). Hydrogen atoms are omitted for clarity. The noncoordinated perchlorate anions are not axial.

Complex Formation Kinetics. When each tetrathiaether was mixed with $Ni(ClO_4)_2$ in acetonitrile, only one kinetic process was observed, which was attributed to the reversible reaction

$$Ni^{2+} + L \underset{k_d}{\overset{k_f}{\rightleftharpoons}} NiL^{2+} \qquad (1)$$

All complex formation reactions were studied under pseudo-first-order conditions with Ni(II) in large excess for which the rate expression may be written as[26]

$$\frac{d[NiL^{2+}]}{dt} = k_f[Ni^{2+}][L] - k_d[Ni^{2+}] = k_{obs}[L] \qquad (2)$$

At the concentrations utilized, the reaction half-lives for the formation of all macrocyclic ligand complexes were in the range 1−100 s, while for Me_2-2,3,2-S_4 the experimental half-lives were in the 100 ms range. The observed pseudo-first-order rate constant, k_{obs}, was plotted as a function of $[Ni^{2+}]_0$ to yield k_f as the slope and k_d as the intercept:[14,27]

$$k_{obs} = k_f[Ni^{2+}]_0 + k_d \qquad (3)$$

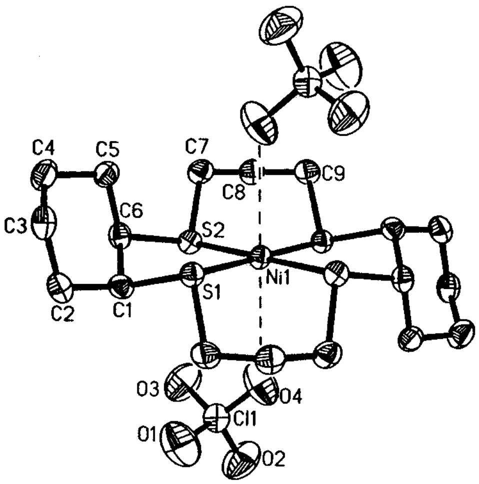

Figure 3. ORTEP drawing showing the structure of the cationic unit for $[Ni^{II}$(*anti-cis,cis*-dicyhx-[14]aneS_4)]$(ClO_4)_2$ (i.e., Ni^{II}(**L8**)). The Ni(II)−O bond distances to the axial perchlorates exceed 2.9 Å. Hydrogen atoms are omitted for clarity.

For the reaction of Ni^{2+} with [14]aneS_4 (**L0**), the complex was sufficiently unstable under the conditions used to yield a significant intercept when the data were plotted using eq 3. This permitted a direct evaluation of k_d. For all other macrocyclic systems studied, the intercepts were insufficient to provide reliable k_d values by this approach. The resolved values of k_f for all nine complexes included in this work are listed in Table 1.

Copper Exchange Kinetics. For all Ni(II)−macrocyclic tetrathiaether complexes, the dissociation kinetics were

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(26) Steinfeld, J. I.; Francisco, J. F.; Hase, W. L. *Chemical Kinetics and Dynamics*, 2nd ed.; Prentice Hall: Upper Saddle River, NJ, 1999; pp 23−24.

(27) Ambundo, E. A.; Deydier, M.-V.; Ochrymowycz, L. A.; Rorabacher, D. B. *Inorg. Chem.*, in press.

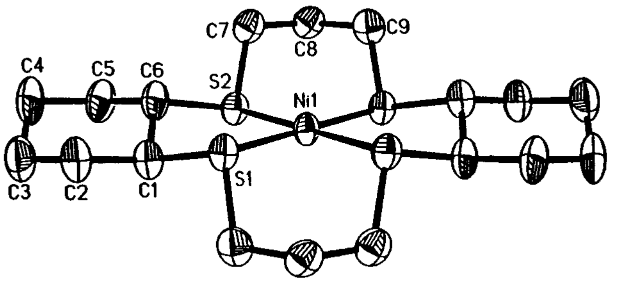

Figure 4. ORTEP drawing showing the structure of the cationic unit for [Ni^{II}(*meso-trans,trans*-dicyhx-[14]aneS$_4$)](ClO$_4$)$_2$ (i.e., Ni^{II}(**L9**)). Hydrogen atoms are omitted for clarity. The noncoordinated perchlorate anions are not axial.

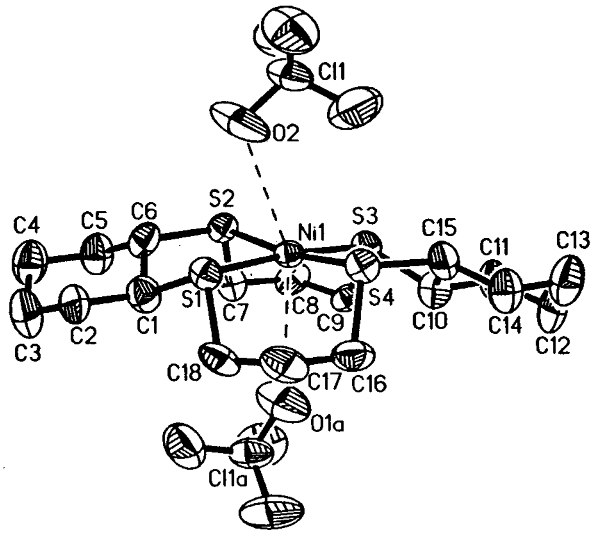

Figure 5. ORTEP drawing showing the structure of the cationic unit for [Ni^{II}(DL-*trans,trans*-dicyhx-[14]aneS$_4$)](ClO$_4$)$_2$ (i.e., Ni^{II}(**L10**)). The Ni(II)−O bond distances to the slightly off-axial perchlorates exceed 2.9 Å. Hydrogen atoms are omitted for clarity.

determined independently using Cu(II) ion as a scavenger:

$$\mathrm{Cu^{2+} + NiL^{2+} \rightarrow CuL^{2+} + Ni^{2+}} \qquad (4)$$

Solutions containing ligand and excess Ni(II) were first equilibrated for a minimum of 1 h to ensure complete complexation.[28] Copper(II) solutions in 10- to 100-fold excess (relative to total ligand) were reacted with the equilibrated NiL^{2+} solution to yield a pseudo-first-order rate constant, k_{app}. Since the CuL^{2+} stability constants in acetonitrile are 10^9 larger than those for the corresponding NiL^{2+} complexes,[17] all reactions proceeded to completion. The reaction of solvated Cu^{2+} with the dissociated ligand in acetonitrile was too fast to measure by the stopped−flow method at 25 °C and, thus, did not influence the observed kinetics. The overall kinetic expression can be represented as[16,29,30]

$$-\frac{\mathrm{d[NiL^{2+}]}}{\mathrm{d}t} = k_\mathrm{d}[\mathrm{Ni^{2+}}] + k_\mathrm{Cu}{}^\mathrm{NiL}[\mathrm{NiL^{2+}}]\,[\mathrm{Cu^{2+}}] = k_\mathrm{app}[\mathrm{NiL^{2+}}] \qquad (5)$$

$$k_\mathrm{app} = k_\mathrm{d} + k_\mathrm{Cu}{}^\mathrm{NiL}[\mathrm{Cu^{2+}}]_0 \qquad (6)$$

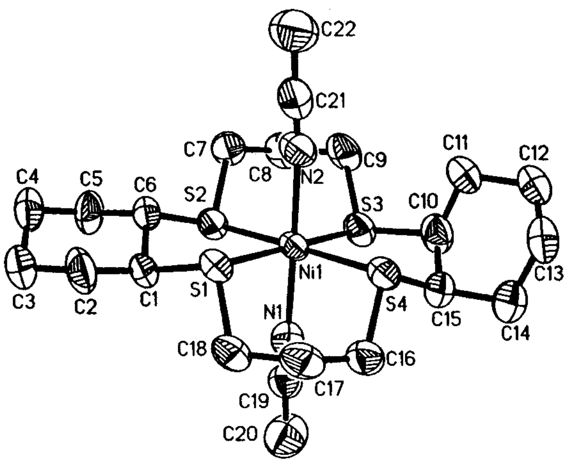

Figure 6. ORTEP drawing showing the structure of the cationic unit for [Ni^{II}(*cis,trans*-dicyhx-[14]aneS$_4$)(CH$_3$CN)$_2$](ClO$_4$)$_2$ (i.e., Ni^{II}(**L11**)). The axially coordinated acetonitriles indicate that this is a high-spin complex. Hydrogen atoms are omitted for clarity.

For three of the more stable complexes (**L8**, **L9**, **L10**), the pseudo-first-order rate constant, k_{app}, showed a dependency on the Cu^{2+} concentration, indicating the formation of a dinuclear NiLCu^{4+} intermediate species (analogous to CuLHg^{4+} reported in previous studies of Cu(II) complex dissociation with Hg(II) ion as scavenger).[16,29,30] For such reactions, extrapolation of k_{app} to $[\mathrm{Cu^{2+}}]_0 = 0$ yielded k_d for the Cu(II)-independent reaction pathway:[16,29,30]

$$\mathrm{NiL^{2+} \rightarrow Ni^{2+} + L} \qquad k_\mathrm{d}$$

$$\mathrm{Cu^{2+} + L \rightarrow CuL^{2+}} \qquad \text{fast}$$

For Ni^{II}([14]aneS$_4$), a huge excess of Ni(ClO$_4$)$_2$ (1.0 M) was utilized to force the NiL^{2+} complex to be fully formed. Thus, these solutions contained 2.0 M ClO$_4^-$ (μ = 3.0 M). This is noteworthy because, in earlier studies of the dissociation of Cu(II)−macrocyclic tetrathiaether complexes in aqueous solution,[16,29] the k_d values *decreased* dramatically with increasing [ClO$_4^-$], attributable to the formation of a perchlorate adduct. This phenomenon is obviously not a factor for the Ni(II) dissociation reactions because the use of Cu(II) as a scavenger in 2.0 M ClO$_4^-$ yielded $k_d = 0.17$ s^{-1}, which is *larger* than the value of $k_d = 0.12$ s^{-1} obtained from the formation study for which [ClO$_4^-$] was maintained at 0.15 M. In the case of the *cis*- and *trans*-cyhx-[14]aneS$_4$ (**L2** and **L3**) complexes, smaller but significant amounts of excess Ni(ClO$_4$)$_2$ (0.10 and 0.040 M, respectively) were added, leading to ionic strength levels of 0.45 and 0.27 M. The k_d values determined for all eight macrocyclic ligand systems are included in Table 1.

Discussion

Structures. The previously reported crystal structures of the Ni(II) complexes formed with **L0**,[20] **L2**, and **L3**[21] showed the metal ion to be four-coordinate with a square-planar geometry, indicative of a low-spin state. For all three complexes the lone electron pairs on the sulfurs were oriented + − − + relative to the macrocyclic ring to generate the *trans*-**III** conformer in which the two propylene bridges extend on opposite sides of the Ni^{II}S$_4$ plane. The crystal structures in Figures 2−5 show that the Ni(II) complexes with four of the dicyclohexanediyl

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(28) For the previous stability constant measurements (ref 17), solutions allowed to equilibrate for 1 h and for 24 h gave identical results. Therefore, it was concluded that complete equilibration was achieved within 1 h.

(29) Diaddario, L. L., Jr.; Ochrymowycz, L. A.; Rorabacher, D. B. *Inorg. Chem.* **1992**, *31*, 2347−2353.

(30) Aronne, L.; Yu, Q.; Ochrymowycz, L. A.; Rorabacher, D. B. *Inorg. Chem.* **1995**, *34*, 1844−1851.

derivatives of [14]aneS_4, that is, with **L7**−**L10**, are also four-coordinate square-planar, although two of these (**L7** and **L10**) have the lone electron pairs of all sulfurs oriented in the same direction (i.e., $++++$) to form the so-called *trans*-**I** conformer in which the two propylene bridging groups lie on the same side of the $Ni^{II}S_4$ plane. As a unique exception, the Ni^{II}(**L11**) adopts a six-coordinate geometry in which acetonitrile molecules occupy the two apical sites (Figure 6). For all five complexes, the S−Ni(II)−S bond angles are close to 90° as shown in Table 3. For the complexes with **L7**, **L10**, and **L11**, internal ligand strain forces the four sulfur donor atoms to be twisted slightly, but the Ni(II) is within 0.03 Å of the average S_4 plane in all cases (Table 3).

Regardless of the conformer adopted, the data in Table 3 show that all Ni(II)−S bond lengths are within the narrow range 2.18−2.20 Å for the four low-spin complexes, in close agreement with the earlier data for the **L0**, **L2**, and **L3** complexes.[20,21] For six-coordinate Ni^{II}(**L11**), these bonds lengthen to 2.32−2.33 Å, identical to the bond lengths found in the similar five- or six-coordinate Cu(II)−tetrathiaether complexes,[31] consistent with the fact that one electron is in the $d_{x^2-y^2}$ orbital in both cases. For the complexes with **L8** and **L10**, the perchlorate anions in the crystal lattice lie near the vacated axial sites of the Ni(II) complex, as shown in Figures 3 and 5; however, the Ni(II)−O bond distances exceed 2.9 Å and have no significant influence on the cationic complex.

Of the corresponding macrocyclic tetramine complexes, Hancock and co-workers[32] reported the structure of [Ni^{II}([14]aneN_4)$(NO_3)_2$] ([14]aneN_4 = cyclam or **L0′**) while Kobiro and co-workers[33] determined the structures of the $Ni(NO_3)_2$ complexes with several derivatives of [14]aneN_4 including **L3′**, **L7′**, and **L8′** (the primes representing the nitrogen analogues of **L3**, **L7**, and **L8**). The Ni(II) complexes with **L0′**, **L3′**, and **L8′** were six-coordinate high-spin in the solid state with apically coordinated nitrate ions, while those involving **L7′** and two related tetramine macrocycles (with tetramethyl substitution on one or both ethylene bridges of **L0′**) were low-spin. Regardless of the spin state, however, all complexes adopted the *trans*-**III** conformation except for Ni^{II}(**L7′**), which, like its tetrathiaether counterpart (Figure 2), was in the *trans*-**I** conformation. Kobiro et al. concluded that steric crowding favors the formation of low-spin complexes. *This rationale cannot account for our observations*, however, since the high-spin Ni^{II}(**L11**) complex must be more sterically crowded than the complexes with **L0**,[20] **L2**, and **L3**,[21] which are low-spin.

Spin State in Solution. On the basis of unspecified spectral comparisons, Kobiro et al.[33] claimed that all Ni(II) macrocyclic tetramine complexes that were low-spin in the solid state remained low-spin in aqueous solution, while those which were high-spin as solids became mixed high- and low-spin upon dissolution. Rosen and Busch[34] have shown that acyclic and macrocyclic tetrathiaethers, with cavity sizes large enough to circumscribe Ni(II), yield low-spin complexes in nitromethane with a single d−d band in the vicinity of 500 nm with $\epsilon \approx 270$. For six-coordinate polythiaether complexes, these same workers later observed two d−d bands near 600 and 900 nm.[35] (Neither study included the intense charge-transfer bands.) The only one of our complexes that is high-spin in the crystalline state, Ni^{II}(**L11**), has an observable d−d band at 508 nm ($\epsilon \approx 270$) in acetonitrile, identical to Rosen and Busch's low-spin complexes. Since all other Ni(II) tetrathiaether complexes included in the current study exhibit similar spectra, we infer that all are predominantly low-spin in the solution phase.

Contrast in Multiphasic Kinetics for Tetramines and Tetrathiaethers. The formation kinetics of the Ni(II)−tetrathiaether complexes included in this work showed no spectral evidence of multiphasic kinetics. This behavior is in contrast to the observations of Hay and Norman,[9] Hertli and Kaden,[10] and Röper and Elias[11] who reported that for the reactions of solvated Ni(II) with macrocyclic tetramines in acetonitrile, DMF, and DMSO at least two (and often three) reaction processes were apparent, the first process being second order (first order in each reactant) and the others being first order. On the basis of multiple wavelength analysis, Sanzenbacher and Elias[12,13] identified and resolved three successive rate constants for Ni(II) reacting with substituted macrocyclic tetramines in DMF. All of these workers concur that the initial second-order process corresponds to either first- or second-bond formation as the rate-determining step, while the slower first-order reactions represent a rearrangement of the ligand around the metal ion to form the thermodynamically stable product.

Although no multiphasic kinetics were observed directly in our studies of the tetrathiaethers, the absence of such observations does not rule out the possibility that such processes might be occurring. Therefore, we undertook the independent determination of the complex dissociation kinetics in the current investigation as described in Results. With the possible exception of Ni^{II}(**L3**), the measured k_f/k_d ratio was found to be in close agreement with the previously measured stability constant, $K_{Ni^{II}L}$,[17] as shown in Table 1. From this we conclude that no unobserved successive reactions are occurring in our complex formation reactions.

Conformational Rearrangement Processes. On the basis of a detailed analysis of macrocyclic ligand coordination reactions, as illustrated in Figure 7,[30] it is apparent that the reaction between Ni(II) and a quadridentate macrocycle must initially yield a folded (cis) complex such as **E-II**. To form the most stable conformer, subsequent steps require (i) an inner-sphere rearrangement to place all four ligand donor atoms in the same plane, as represented by **F-II** (a trans conformer) followed by (ii) the inversion of one or two donor atoms (depending on the initial conformer formed) to yield one of the two stable conformers, **F-I** (*trans*-**I**) or **F-III** (*trans*-**III**).[36−38] For nitrogen donor atoms, inversion is facilitated by the abstraction of a hydrogen ion to form a temporary amide ion, following which the nitrogen can invert and reprotonate (Figure 8A). Since hydrogen ion abstraction is not a facile process in solvents with poor protophilicity[39] such as acetonitrile, DMF, and DMSO, slow inversion of two nitrogen donor atoms would account for the two slow steps and the general base catalysis demonstrated by Hay and Norman[9] and later elaborated by Sansenbacher and Elias.[12,13]

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(31) Pett, V. B.; Diaddario, L. L., Jr.; Dockal, E. R.; Corfield, P. W.; Ceccarelli, C.; Glick, M. D.; Ochrymowycz, L. A.; Rorabacher, D. B. *Inorg. Chem.* **1983**, *22*, 3661−3670.

(32) Thöm, V. J.; Fox, C. C.; Boeyens, J. C. A.; Hancock, R. D. *J. Am. Chem. Soc.* **1984**, *106*, 5947−5955.

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(36) (a) Adam, K. R.; Atkinson, I. M.; Lindoy, L. F. *Inorg. Chem.* **1997**, *36*, 480−481. (b) Adam, K. R.; Antolovich, M.; Brigden, L. G.; Lindoy, L. F. *J. Am. Chem. Soc.* **1991**, *113*, 3346−3351.

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(38) Cooper, C. G.; Zimmer, M. *Struct. Chem.* **1999**, *10*, 17−27.

(39) The term "protophilic" refers to solvents that can accept a hydrogen ion. Bates, R. G. *Determination of pH: Theory and Practice*, 2nd ed.; Wiley: New York, 1973; p 173.

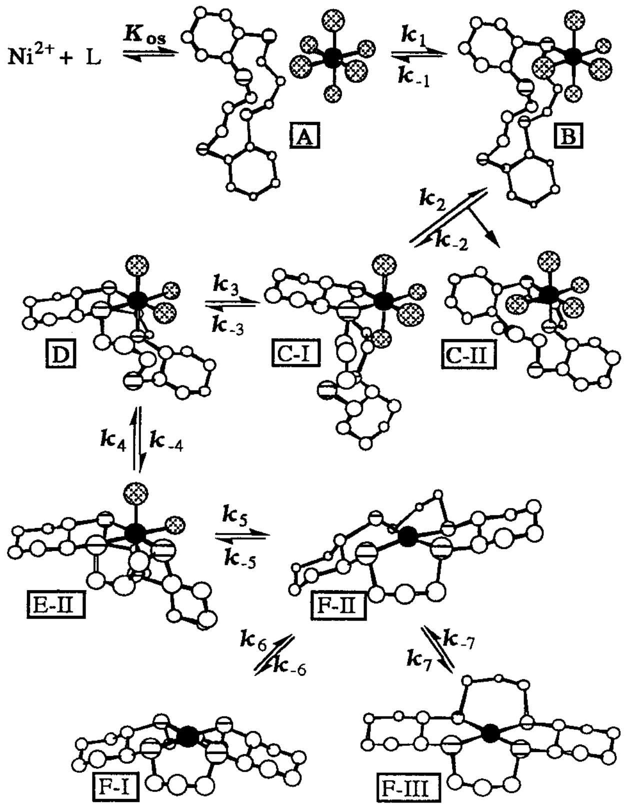

Figure 7. Schematic representation of the stepwise formation reaction of $Ni(CH_3CN)_6^{2+}$ reacting with a macrocyclic tetrathiaether ligand. The *meso-trans,trans*-dicyhx-[14]aneS$_4$ (**L9**) ligand is represented here for purposes of illustration. The solid circle represents the nickel atom, the crosshatched circles are the nitrogen atoms of CH_3CN (the carbons being omitted for clarity), the horizontally striped circles are the sulfur donor atoms, and the open circles are carbon atoms of the macrocycle (all hydrogen atoms being omitted for clarity). Conformers **F-I** and **F-III** are shown as low-spin four-coordinate species on the basis of crystal structures and spectral evidence. Conformer **F-II** is also presumed to be four-coordinate for Ni(II).

Although similar conformational rearrangements must be required in the case of the macrocyclic tetrathiaether complexes,[30] the sulfur atoms have two lone electron pairs (one of which is coordinated to the metal ion) so that inversion can occur without hydrogen ion abstraction or bond dissociation, as illustrated schematically in Figure 8B. Therefore, we assume that conformational rearrangement is a facile process in the case of the macrocyclic tetrathiaethers (even in nonprotophilic solvents) relative to the overall rate of Ni(II) complex formation. The absence of multiphasic kinetics is then attributed to this facile rearrangement.

Analysis of the Reaction Kinetics. As listed in Table 1, all formation rate constants for Ni(II) reacting with the macrocyclic tetrathiaethers lie within a 4-fold range. Interestingly, the extreme values are obtained for the two *cis,cis*-dicyhx-[14]aneS$_4$ complexes, with the syn-cis,cis derivative (**L7**) being the largest. The lone acyclic ligand complex, Ni^{II}(Me$_2$-2,3,2-S$_4$), has a k_f value that is about an order of magnitude larger than those for the macrocyclic complexes. This same general trend in k_f values was observed earlier for the reaction of Cu(II) ion with this same set of ligands in 80% methanol,[30] including noticeably larger k_f values for the reactions with Me$_2$-2,3,2-S$_4$ and with ligand **L7** (see Figure 9A). This trend is in sharp contrast to that of the formation rate constants for Ni(II) reacting with corresponding tetramines in acetonitrile, as reported by Hay and Norman.[9] Not only were all of their formation rate constants significantly larger than ours but they also observed *no significant difference* in the k_f values for corresponding *acyclic* and *cyclic* ligands.

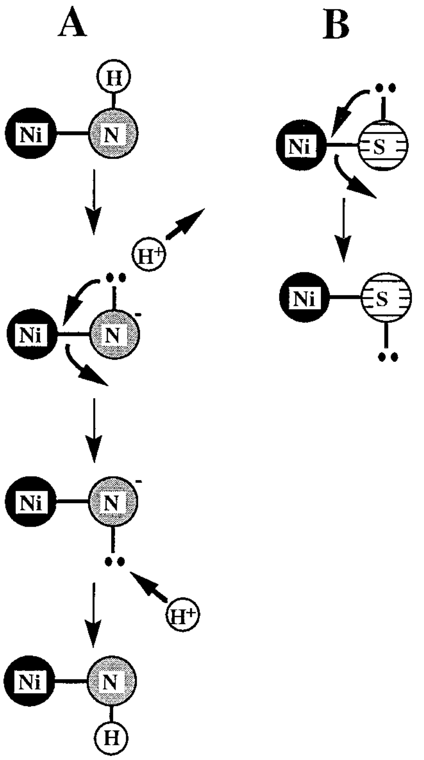

Figure 8. Schematic representation of the process involved in inverting coordinated donor atoms without undergoing coordinate-bond dissociation. For a coordinated amine nitrogen (A) the hydrogen must first be removed to create a temporary amide prior to inversion. Hydrogen ion abstraction is not required to invert a thiaether sulfur (B). For clarity, the remaining coordinate bonds to the Ni(II) and the covalent bonds of the nitrogen and sulfur atoms to the adjacent carbon atoms are omitted.

For the mechanism illustrated in Figure 7, the stepwise process leading to completion of the first chelate ring may be represented as

$$\mathrm{Ni}^{2+} + \mathrm{L} \overset{K_{os}}{\rightleftharpoons} \mathrm{A} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{B} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \mathrm{C} \qquad (7)$$

where A represents the outer-sphere (nearest-neighbor) complex, B represents the singly bonded complex, and C represents the doubly bonded complex (see Figure 7). If $k_2 \gg k_{-1}$, the first bond-formation step, represented by rate constant k_1, should be rate-determining, and the overall observed formation rate constant can be represented as[40]

$$k_f = K_{os} k_1 \qquad (8)$$

Treating each multidentate ligand as "a donor atom with a tail",[41] the value of K_{os} for a solvated Ni(II) ion and a specific donor atom can be estimated from the modified Fuoss equation[42]

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(40) Wilkins, R. G. *Kinetics and Mechanism of Reactions of Transition Metal Complexes*, 2nd ed.; VCH: Weinheim, Germany, 1991; pp 205−208.

(41) Lin, C.-T.; Rorabacher, D. B. *Inorg. Chem.* **1973**, *12*, 2402−2410. For the "donor atom with a tail" concept, see p 2406, column 2.

(42) Fuoss, R. M. *J. Am. Chem. Soc.* **1958**, *80*, 5059−5061. Eigen, M.; Kruse, W.; Maass, G.; DeMaeyer, L. *Prog. React. Kinet.* **1964**, *2*, 285−318.

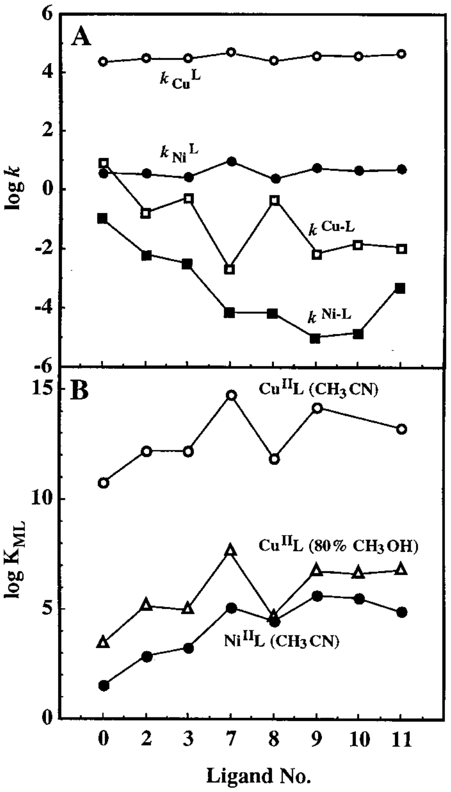

Figure 9. (A) Trends in the logarithmic formation rate constants for solvated Cu(II), $k_{Cu}{}^{L}$ (open circles), and for solvated Ni(II), $k_{Ni}{}^{L}$ (solid circles), reacting with eight macrocyclic tetrathiaethers. The corresponding logarithmic dissociation rate constants k^{Cu-L} (open squares) and k^{Ni-L} (solid squares) are also represented. The Cu(II) rate constants were determined in 80% methanol−20% water (w/w), while the Ni(II) rate constants were determined in acetonitrile. All data were taken at 25 °C. (B) Corresponding logarithmic stability constants for the Cu(II) macrocyclic tetrathiaether complexes in 80% methanol−20% water (w/w) and in acetonitrile and the Ni(II) complex stability constants in acetonitrile. All data were taken at 25 °C.

as applied to uncharged ligands:[43]

$$K_{os} = \frac{4}{3}\pi a^3 N_A 10^{-3} \tag{9}$$

In this expression, a represents the center-to-center distance of closest approach (in cm) between the solvated metal ion and a donor atom of the ligand in the outer-sphere complex, and N_A represents Avogadro's number. For reactions involving Ni(H_2O)$_6{}^{2+}$, a value of 4 × 10^{-8} cm has been applied for the center-to-center distance of closest approach to simple unidentate ligands such as ammonia, yielding $K_{os} = 0.16$ M^{-1}.[43] For the larger Ni(CH_3CN)$_6{}^{2+}$ and Ni(DMF)$_6{}^{2+}$ ions considered in this discussion, molecular models indicate that the value of a increases to approximately 6 × 10^{-8} and 7.5 × 10^{-8} cm, respectively, resulting in K_{os} values of approximately 0.54 and 1.1 M^{-1}.

Many studies have shown that inner-sphere substitution on Ni(H_2O)$_6{}^{2+}$ occurs by a dissociative interchange (I_d) process,[2,3,40,43] and the same mechanism is anticipated in acetonitrile and DMF because solvent exchange on Ni(II) has a positive volume of activation in those solvents as well.[18,44] As a result, the value of k_1 should depend on the rate constant for inner-sphere solvent exchange (Eigen−Wilkins mechanism), k_{ex}, for which values of 3.15 × 10^4,[44] 2.8 × 10^3,[18] and 3.8 × 10^3 s^{-1} [18] have been determined at 25 °C in water, acetonitrile, and DMF, respectively. Thus, the theoretical rate constant for first-bond formation as the rate-determining step in each of these three solvents can be represented as

$$k_f = K_{os}(^3/_4)k_{ex}\rho \tag{10}$$

In eq 10, the $^3/_4$ factor is based on a model in which eight outer-sphere species (including solvent molecules) are presumed to be situated over the octahedral faces and are competing for the six inner-sphere coordination sites.[45,46] The "ρ" term is introduced as an apparent steric factor for substituted donor atoms to account for the fact that many configurations of the ligand in the outer-sphere complex do not have a donor atom oriented in such a way as to be able to compete with the adjacent outer-sphere solvent molecules for the vacant (or vacating) site when a Ni−solvent bond dissociates.[27,47] By use of the K_{os} and k_{ex} values cited above, eq 10 yields predicted values of k_f equal to 3.5 × 10^3, 1.13 × 10^3, and 2.3 × 10^3 for Ni(II) complex formation reactions with unhindered donor atoms (i.e., $\rho = 1$) in water, acetonitrile, and DMF, respectively.

The *apparent* value of ρ for any specific ligand can be evaluated according to eq 10 by dividing the experimental k_f value by the coefficients listed above; that is, $\rho = k_f/(1.13 \times 10^3)$ for reactions in acetonitrile. This leads to calculated *experimental* values of $\rho \approx 0.06$ for Me_2-2,3,2-S_4 and $\rho \approx 0.002-0.009$ for the various macrocyclic ligands (see Table 1). As we have recently noted elsewhere,[27] for a solvated metal ion reacting with the terminal sulfurs in Me_2-2,3,2-S_4 (i.e., substituted by a methyl group and an ethyl group or larger), the theoretical ρ value is >0.02 per donor atom or >0.04 if we account for the presence of two terminal donor atoms (based on our "donor atom with a tail" model).[41] These ρ values are based on studies of comparable nitrogen donor ligands[48] and are given here as lower limits because sulfurs are larger than nitrogens and have two unshared electron pairs. For the interior sulfur donor atoms in Me_2-2,3,2-S_4, the ρ value is estimated to be >0.006 per donor atom or >0.012 for both sulfurs. Thus, on the basis of the "donor atom with a tail" concept, the overall *theoretical* ρ value for the reaction of Ni(II) with Me_2-2,3,2-S_4 in acetonitrile is $>(0.04 + 0.012) \gtrsim 0.05$, which is in excellent agreement with the *experimental* ratio of 0.06. From this we conclude that the rate-determining step for the acyclic ligand is at the point of first-bond formation; that is, the k_f value observed for the reaction with this ligand agrees with the value calculated from eq 10 based on our estimation of expected steric factors.

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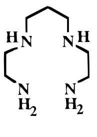
(46) Sokol, L. S. W. L.; Fink, T. D.; Rorabacher, D. B. *Inorg. Chem.* **1980**, *19*, 1263−1266.

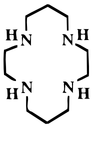
(47) The ρ term introduced here is equivalent to the concept of the "reduction in the solid angle corresponding to reactive encounters" as originally formulated by Kowalak et al. [Kowalak, A.; Kustin, K.; Pasternack, R. F.; Petrucci, S. *J. Am. Chem. Soc.* **1967**, *89*, 3126−3130.]

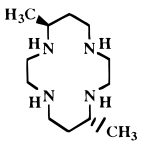
(48) The reference ρ value for a monoalkyl-substituted donor atom (alkyl = ethyl or larger) relative to an unsubstituted donor atom is presumed to be equal to the ratio of formation rate constants for Ni(H_2O)$_6{}^{2+}$ reacting with ethylamine compared to NH_3, i.e., $\rho = 0.2$ [Rorabacher, D. B.; Melendez-Cepeda, C. A. *J. Am. Chem. Soc.* **1971**, *93*, 6071−6076.] In the current discussion, this value is applied to the terminal donor atoms in 2,3,2-tet. For donor atoms substituted by two alkyl groups, the additional steric effect imposed by a second alkyl group (ethyl or larger) on a donor atom is assumed to be equal to the ratio of formation rate constants for Ni(H_2O)$_6{}^{2+}$ reacting with *N,N,N*-trimethylethylenediamine ($tmen^+$) [ref 41] and the monoprotonated species of *N,N'*-diethylethylenediamine [ref 50], viz., 0.006 per available donor atom [cf., ref 27].

For the macrocyclic tetrathiaethers, all donor atoms are substituted by two alkyl groups that are ethyl or larger for which we estimate a ρ value of >0.006 per donor atom[48] or an overall *theoretical* ρ equal to $>0.02_4$ for a quadridentate ligand. Since the *experimental* ρ values are 0.002−0.009 for the macrocyclic tetrathiaether reactions, it would appear that the rate-determining step may have shifted to the point of second-bond formation, particularly for the slower reacting ligands, provided that the steric accessibility of the solvated Ni(II) ion to the sulfur donor atoms in the substituted macrocycles is correctly estimated.

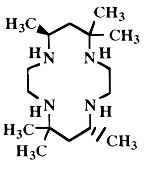
Consideration of Tetramine Rate Constants in Acetonitrile. If eq 10 is applied to the rate constants for $Ni(CH_3CN)_6^{2+}$ reacting with tetramines in acetonitrile, as reported by Hay and Norman,[9] the *experimental* ρ values are 0.9 for 2,3,2-tet and 0.7−0.8 for cyclam (**L0′**) and derivatives thereof.


2,3,2-tet


cyclam (L0')



Me$_2$-cyclam



Me$_6$-cyclam (tet a)

By contrast, the *theoretical* ρ values would be expected to be 0.4 for 2,3,2-tet and 0.02_4 for the macrocyclic tetramines.[48] Whereas the two ρ values for the *acyclic* ligand are in reasonable agreement, the *macrocyclic* tetramines appear to be reacting much more rapidly with $Ni(CH_3CN)_6^{2+}$ than anticipated by the Eigen−Wilkins mechanism. This 30-fold discrepancy indicates that one of the following situations must be operative: (i) polyamine substitution reactions in acetonitrile are not dissociative in nature; (ii) the *theoretical* steric effects, which were based on aqueous amine complexation reactions, are not valid in acetonitrile; (iii) the extent of outer-sphere complex formation is greatly enhanced in acetonitrile compared to the purely statistical model utilized in the Fuoss equation. The first possibility is considered highly unlikely on the basis of the positive volume of activation for solvent exchange as determined by Merbach and co-workers.[18] Although the k_f value reported for Ni(II) reacting with NH_3 in acetonitrile is also anomalously large,[24] this latter value is acknowledged to be in error by a factor of 2 or more. Moreover, the k_f value obtained for Ni(II) reacting with pyridine in acetonitrile[24] is apparently in line with expectations when compared to the corresponding aqueous result.[49] The second possibility, that the application of *theoretical* steric factors derived from aqueous reactions may be inaccurate in acetonitrile, appears unlikely because our data for the reaction of $Ni(CH_3CN)_6^{2+}$ with Me_2-2,3,2-S_4 tend to support the fact that they are of the correct order of magnitude. Under any circumstances, one would expect significant differences in the *experimental* ρ values obtained from the data of Hay and Norman for 2,3,2-tet and the macrocyclic tetramines. This is not observed.

As to the third possibility, it is noteworthy that Chattopadhyay and Coetzee[24] reported several anomalously large k_f values for $Ni(CH_3CN)_6^{2+}$ reacting with bipyridine and related ligands in acetonitrile that they attributed to some type of outer-sphere interaction between the solvated metal ion and nitrogen-containing (or pyridyl-containing) ligands leading to enhanced K_{os} values. This is reminiscent of our earlier observations on accelerated polyamine reactions with Ni(II) in aqueous solution, which we have attributed to hydrogen-bond formation between a nitrogen donor atom in the outer-sphere complex and a coordinated water molecule.[43,50] Such hydrogen bonding would not be expected between an outer-sphere nitrogen of the substituting ligand and an inner-sphere acetonitrile. Whatever the underlying cause, however, the formation rate constants for Ni(II) reacting with the macrocyclic polyamine ligands in acetonitrile are anomalously large, a fact not recognized by Hay and Norman at the time they reported their results. Therefore, we conclude that their rate constants for acyclic and macrocyclic tetramine ligands cannot be interpreted to reflect the influence of ligand cyclization upon complex formation.

Consideration of Tetramine Rate Constants in DMF. For the kinetic studies in DMF involving Ni(II) reacting with Me_2-3,2,3-tet and cyclam, Hertli and Kaden[11] reported k_f values of 3.2×10^3 and 1.8×10^3 M^{-1} s^{-1}, respectively, for the first reaction step at 25 °C and Sanzenbacher and Elias[12] obtained $k_f = 7 \times 10^2$ for the similar reaction with Me_2cyclam. On the basis of the reported inner-sphere solvent exchange rate constant for $Ni(DMF)_6^{2+}$, $k_{ex} = 3.8 \times 10^3$ s^{-1},[18] eq 10 indicates that the *experimental* ρ values associated with these three formation rate constants are approximately 1, 0.6, and 0.2, respectively (based on $K_{os} \approx 1.1$). These values are much larger than the *theoretical* ρ values of 0.05, 0.02, and <0.02, respectively. However, molecular models suggest that *experimental* ρ values may increase in DMF, since a majority of the bulky DMF molecules in the outer-solvation sphere are likely to exist in orientations unfavorable for insertion into vacating inner-sphere sites. Thus, other ligands in the outer sphere may compete more successfully with the outer-sphere solvent molecules for vacated sites than is the case in aqueous solution or other less bulky solvents.

If the foregoing interpretation is applicable, all *theoretical* ρ values calculated by our approach will appear to be too small in DMF, but the relative order of the ρ values (or k_f values) should be correct. In further support of this interpretation, we note that the k_f values for Ni(II) reacting with Me_2-3,2,3-tet, cyclam, Me_2cyclam, and tet-*a* in DMF exhibit ratios similar to the corresponding k_f ratios that we observed previously for these four ligands reacting with $Cu(OH)_3^-$ in aqueous solution.[8]

Comparison of Dissociation Rate Constants for Ni(II)− and Cu(II)−Tetrathiaether Complexes. As illustrated in Figure 9B, the *stability* constants for the Cu(II) complexes with the macrocyclic tetrathiaethers differ by 10^6 in acetonitrile and in 80% methanol,[22] but the trends are virtually identical in both solvents. Since the formation rate constants for the Cu(II) complexes in 80% methanol and the Ni(II) complexes in acetonitrile are relatively constant, as shown in Figure 9A, the stability constants must be inversely proportional to the dissociation rate constants and the relative trends in k_d for Cu(II) must also be independent of the solvent matrix.[30] Furthermore, since the stability constant trends for Ni(II) and Cu(II) show significant differences (Figure 9B), the k_d trends must also differ independent of the solvent.

Solvated Ni(II) is high-spin, and the switch to low-spin during the complex formation process must occur after the point of the rate-determining step, presumably at the point where the macrocyclic ligand assumes planar coordination (species **F-II** in Figure 7). Therefore, the equilibrium constant for spin change should be reflected solely in the dissociation rate constants. However, the contribution of the spin change to the dissociation kinetics may be relatively uniform in all cases.

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(49) (a) Melson, G. A.; Wilkins, R. G. *J. Chem. Soc.* **1962**, 4208−4213. (b) Bulmer, R. S.; Caldin, E. F.; Walton, A. W. *Trans. Faraday Soc.* **1971**, *67*, 3343−3356.

(50) Turan, T. S.; Rorabacher, D. B. *Inorg. Chem.* **1972**, *11*, 288−295.

The addition of a cyclohexane ring to the macrocycle should predispose the ligand toward a more endo conformation, which might be expected to decrease k_d, and a second cyclohexane moiety should then cause a further decrease. These trends are observed for the Ni(II) k_d values in Figure 9B. However, the Cu(II) data show significant aberrations. Some specific features associated with the inconsistencies in the dissociation behavior for these two metal ions are evident in the k^{Cu-L}/k^{Ni-L} ratios, which are 19−150 for the complexes with **L0**, **L2**, **L3**, **L7**, and **L11** but are significantly larger at 570 and 710 for the complexes with two *trans*-cyclohexane moieties (**L9** and **L10**). For the *anti-cis,cis*-dicyhx-[14]aneS_4 (**L8**) systems, a huge ratio of 6.6×10^3 is observed. The large discrepancy in the relative dissociation rate constants for the two *cis,cis*-dicyclohexanediyl macrocycles (**L7** and **L8**) is wholly attributable to the Cu(II) behavior (Figure 9B) and must be ascribed to either (i) significant differences in the structures of the thermodynamically stable conformations or (ii) a greater preference of Cu(II), compared to Ni(II), for the most stable conformation.

Since Cu(II) readily adapts to a square-pyramidal geometry in which the lone pairs on the sulfurs orient in the same direction (+ + + +) relative to the macrocyclic ring. We infer that the relatively small dissociation rate constant for Cu^{II}(*syn-cis,cis*-dicyhx-[14]aneS_4) relates to the reduced strain in the **F-I** conformer, thereby decreasing the K_{-6} ($= k_{-6}/k_6$) equilibrium constant (Figure 7). By contrast, the *trans*-dicyclohexanediyl derivatives (**L9** and **L10**) and, most especially, the *anti-cis,cis* -dicyhx-[14]aneS_4 cannot easily adopt this conformation, so these complexes form exceptionally labile Cu(II) complexes.

Conclusions

For the current studies, the ratios of the formation to the dissociation rate constants for the Ni(II)−tetrathiaether complexes in acetonitrile are in good agreement with the thermodynamic stability constants, indicating that only a single reaction process can be distinguished. First-bond formation appears to represent the rate-determining step for $Ni(CH_3CN)_6^{2+}$ reacting with the acyclic ligand, Me_2-2,3,2-S_4. The decreased formation rate constants for the macrocyclic tetrathiaethers imply that the rate-determining step has shifted to the point of chelate ring closure, as previously deduced for the reactions of these same ligands with Cu(II) in methanol−water mixtures.[14,30] Subsequent conformational reorganization is apparently rapid.

The differing trends in the stability constants of the various dicyclohexane derivatives of [14]aneS_4 with Cu(II) and Ni(II)[17] appear to be almost wholly reflected in the dissociation rate constants. We suggest that these represent differences in the stable conformations adopted by some of these ligands that we attribute to the ability of Cu(II) to adapt to a five-coordinate square-pyramidal geometry, whereas Ni(II) prefers to be square-planar.

Comparison of the Ni(II)−tetrathiaether complexation rate constants in acetonitrile with similar data for tetramines in this and other solvents reveals some significant differences. In particular, the macrocyclic tetramine complexation reactions in acetonitrile appear to be anomalously fast relative to all other data sets examined. By contrast, the formation kinetics of solvated Ni(II) with acyclic and macrocyclic tetramines in DMF and similar data with $Cu(OH)_3^-$ in basic aqueous media show trends similar to those observed for the corresponding tetrathiaethers in acetonitrile, although the DMF data suggest that outer-sphere ligands compete more favorably for vacant inner-sphere sites than is the case in less bulky solvents.

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Supporting Information Available: Five X-ray crystallographic files, in CIF format, and two tables listing kinetic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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