Contribution from the Department of Chemistry,
Purdue University, West Lafayette, Indiana 47907

Ligand Solvation and the Macrocyclic Effect. A Study of Nickel(II)-Tetramine Complexes

FREDERICK P. HINZ and DALE W. MARGERUM*

Received April 18, 1974 AIC40252N

The stability constant for the cyclic tetramine-nickel complex with 5,6,5,6-membered chelate rings is more than 10^6-fold greater than the constant for the corresponding open-chain tetramine complex with 5,6,5-membered chelate rings. As two to six methyl substituents are placed on carbon atoms in the six-membered chelate rings of the macrocyclic complexes, the stability constants decrease by factors of 2 to 10^4. The enhanced stability with the cyclic *vs.* open-chain ligand (the macrocyclic effect) is almost entirely due to more favorable $\Delta H°$, but the nickel-amine bond strengths are not significantly different. The enthalpic differences are attributable to the decreased ligand solvation of the macrocycle which has less amine-hydrogen-bonded water to be displaced in complex formation. The more favorable configurational entropy built into the macrocyclic ligand tends to be offset by less water being released from the solvated ligand. This type of ligand solvation effect will be important for any system where strong solvation is possible and the donor groups are forced to be close to one another.

Introduction

The enhanced stability of the copper(II) complex of a 14-membered cyclic tetramine ligand as compared to an open-chain tetramine ligand has been termed the *macrocyclic effect.*[1] The present study shows similar enhanced stability constants for nickel(II) complexes. In earlier work it was suggested that differences in the configuration and solvation of the free macrocyclic ligand compared to the noncyclic ligand contributed to the macrocyclic effect.[1] The relative importance of these factors is considered in this work from measurements of the enthalpy for the formation reactions of the nickel(II) complexes. In addition, the effect of *C*-methyl substituents on the stabilities of the macrocyclic ligand complexes is determined.

The traditional method of proton *vs.* metal ion competition for the ligand in order to determine stability constants is not satisfactory with the macrocyclic complexes because the complexes are very stable and because the rates of formation and dissociation are exceedingly slow. Even a labile metal ion such as Cu(II) required several months to reach equilibrium with macrocyclic ligands in hydrochloric acid solutions. Furthermore, high concentrations of HCl were required and all four of the protonation constants of the ligand were needed.[1] The tetramine macrocyclic complexes of Ni(II) are virtually inert to acid dissociation, so this method cannot be used. Cyanide ion, however, reacts relatively rapidly to remove nickel ion from its macrocyclic complexes.[2] The use of cyanide ion competition with the macrocyclic for nickel ion (eq 1) has additional advantages. The

$$\mathrm{NiL^{2+} + 4CN^- \rightleftarrows Ni(CN)_4{}^{2-} + L} \tag{1}$$

reactions can be studied in 0.1 *M* NaOH where there is very little protonation of the macrocyclic ligand. The large molar absorptivity of $\mathrm{Ni(CN)_4{}^{2-}}$ permits low concentrations to be used, thus reducing problems from the limited solubility of some of the free ligands. Although $\mathrm{NiLCN^+}$ and $\mathrm{NiLOH^+}$ species do form and must be taken into account, the stability constants of these adducts can be measured spectrophotometrically in separate experiments. Finally, the heat of formation of $\mathrm{Ni(CN)_4{}^{2-}}$ has been determined,[3] as well as its stability constant,[4] so that additional calorimetric measurements and/or equilibrium measurements of eq 1 at various temperatures permit the calculation of the $\Delta H°$ and $\Delta S°$ values for the formation of $\mathrm{NiL^{2+}}$ from $\mathrm{Ni^{2+}}$ and L. A comparison of the thermodynamic data for $\mathrm{Ni(2,3,2\text{-}tet)^{2+}}$ and $\mathrm{Ni(cyclam)^{2+}}$ (or $\mathrm{[14]aneN_4Ni^{II}}$) indicates the importance of ligand solvation in the macrocyclic effect. The structures of the ligands are given in Figure 1 along with the systematic abbreviations[5] used for the names of the macrocyclic ligands. Other frequently used abbreviations are given in parentheses.

Experimental Section

Reagents. The ligand $\mathrm{[14]aneN_4}$ was prepared by a combination of the procedures of Bounsall and Koprich[6] and Bosnich, Poon, and Tobe.[7] The ligands C(5,12)-*ms*-$\mathrm{Me_2[14]aneN_4}$[8] and C(5,12)-*rac*-$\mathrm{Me_6[14]aneN_4 \cdot H_2O}$[9] were prepared by published methods. Melting points for all ligands were consistent with the published values and the carbon, hydrogen, and nitrogen analyses agreed with the theoretical compositions. Purified 2,3,2-tet was obtained from the commercial product (Eastman) by a method developed for purification of other polyamines.[10] It was vacuum distilled with a major fraction collected at 94-96° under 0.07 mm pressure. Its purity was confirmed by gas chromatographic analysis.[11] The perchlorate salts of the nickel(II) complexes of $\mathrm{[14]aneN_4}$,[12] C(5,12)-*rac*-$\mathrm{Me_6[14]aneN_4}$,[2,13] and C(5,12)-*ms*-$\mathrm{Me_6[14]aneN_4}$[2,13] were prepared by published methods. Crystals of $\mathrm{[Ni(C(5,12)\text{-}}$*ms*$\mathrm{\text{-}Me_2[14]aneN_4)](ClO_4)_2}$ were prepared by the addition of the macrocyclic ligand to a solution of Ni(II) in excess ammonia at 60°. After warming for 1 hr, the solution was cooled, acidified, and $\mathrm{NaClO_4}$ was added to bring the complex out of solution. The complex was recrystallized twice from methanol. The nickel(II) complex of 2,3,2-tet was obtained by the addition of a slight excess of $\mathrm{Ni(ClO_4)_2 \cdot 6H_2O}$ in ethanol to a solution of 2,3,2-tet in ethanol. The mixture was stirred for 3 hr to ensure complete conversion to $\mathrm{[Ni(2,3,2\text{-}tet)](ClO_4)_2}$. The crystals were isolated by filtration, dissolved in cold acetone, refiltered, and isolated by filtration after the addition of ethyl ether. The product was recrystallized twice from methanol. The sodium salt of $\mathrm{Ni(CN)_4{}^{2-}}$ was isolated from aqueous solution as $\mathrm{Na_2Ni(CN)_4 \cdot 3H_2O}$. *Anal.* Calcd for $\mathrm{[14]aneN_4Ni^{II}(ClO_4)_2}$: C, 26.2; H, 5.2; N, 12.2; Cl, 15.1. Found: C, 26.4; H, 5.5; N, 12.1; Cl, 15.5. Calcd for C(5,12)-*ms*-$\mathrm{Me_2[14]aneN_4Ni^{II}(ClO_4)_2}$: C, 29.7; H, 5.8; N, 11.5. Found: C, 29.7; H, 6.0; N, 11.4. Calcd for C(5,12)-*rac*-$\mathrm{Me_6}$[14]-

---

[1] D. K. Cabbiness and D. W. Margerum, *J. Amer. Chem. Soc.*, 91, 6540 (1969).

[2] N. F. Curtis, *J. Chem. Soc.*, 2644 (1964).

[3] J. J. Christensen, R. M. Izatt, J. D. Hale, R. T. Pack, and G. D. Watt, *Inorg. Chem.*, 2, 337 (1963).

[4] G. B. Kolski and D. W. Margerum, *Inorg. Chem.*, 7, 2239 (1968).

[5] J. F. Endicott, N. A. P. Kane-Maguire, D. P. Rillema, and T. S. Roche, *Inorg. Chem.*, 12, 1818 (1973).

[6] E. J. Bounsall and S. P. Koprich, *Can. J. Chem.*, 48, 1481 (1970).

[7] B. Bosnich, C. K. Poon, and M. L. Tobe, *Inorg. Chem.*, 4, 1102 (1965).

[8] R. A. Kolinski and B. Korybut-Daszkiewicz, *Bull. Acad. Pol. Sci., Ser. Sci. Chim.*, 17, 13 (1969).

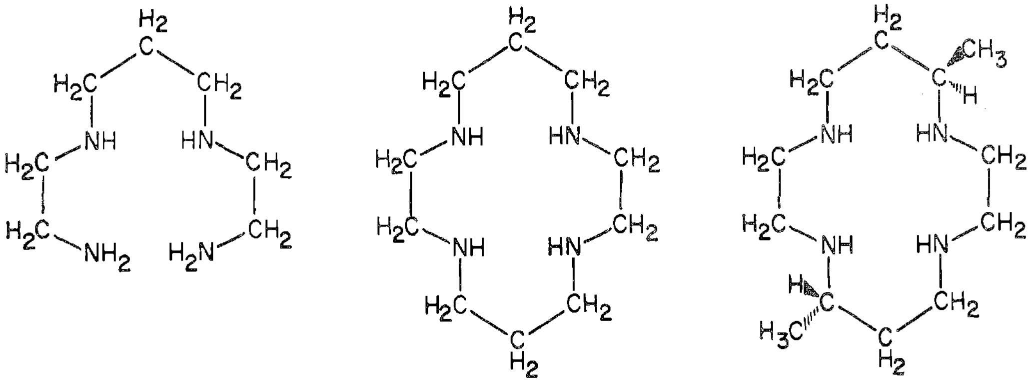
[9] P. O. Whimp and N. F. Curtis, *J. Chem. Soc. A*, 867 (1966).

[10] C. N. Reilley and A. Vavoulis, *Anal. Chem.*, 31, 243 (1959).

[11] G. M. Hodgson, Ph.D. Thesis, Purdue University, West Lafayette, Ind., 1972, p 82.

[12] B. Bosnich, M. L. Tobe, and G. A. Webb, *Inorg. Chem.*, 4, 1109 (1965).

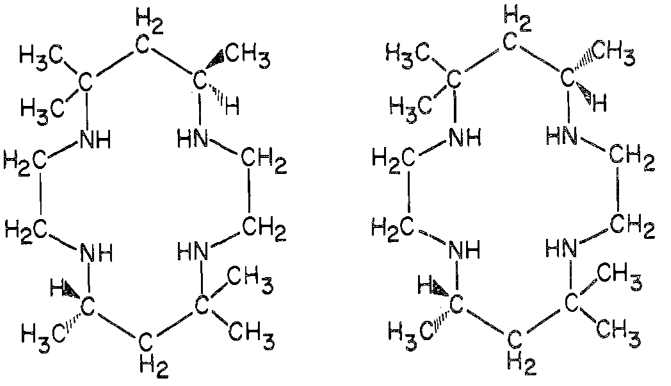
[13] N. F. Curtis, *J. Chem. Soc.*, 924 (1965).



2,3,2-tet
N,N'-bis(2-aminoethyl)-1,3-propanediamine

[14]aneN$_4$
(cyclam)
1,4,8,11-tetraazacyclotetradecane

C(5,12)-*ms*-Me$_2$[14]aneN$_4$
(Me$_2$cyclam)
meso-5,12-dimethyl-1,4,8,11-tetraazacyclotetradecane



C(5,12)-*ms*-Me$_6$[14]aneN$_4$
(tet *a*)
meso-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane

C(5,12)-*rac*-Me$_6$[14]aneN$_4$
(tet *b*)
rac-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane

Figure 1. Tetramine ligands used in this study with systematic (and previously used) abbreviations.

aneN$_4$Ni^{II}(ClO$_4$)$_2$: C, 35.4; H, 6.7; N, 10.3. Found: C, 35.5; H, 6.8; N, 10.5. Calcd for C(5,12)-*ms*-Me$_6$[14]aneN$_4$Ni^{II}(ClO$_4$)$_2$: C, 35.4; H, 6.7; N, 10.3. Found: C, 35.6; H, 6.7; N, 10.1. Calcd for 2,3,2-tetNi^{II}(ClO$_4$)$_2$: C, 20.1; H, 4.8; N, 13.4; Cl, 17.0. Found: C, 20.3; H, 4.7; N, 13.4; Cl, 17.0. Calcd for Na$_2$Ni(CN)$_4$·3H$_2$O: C, 18.2; H, 2.3; N, 21.3. Found: C, 18.4; H, 2.6; N, 21.0. Calcd for 14[ane]N$_4$: C, 60.0; H, 12.0, N, 28.0. Found: C, 60.2; H, 11.9; N, 28.1. Calcd for C(5,12)-*ms*-Me$_2$[14]aneN$_4$: C, 63.2; H. 12.3; N, 24.6. Found: C, 63.3; H, 12.4; N, 24.4. Calcd for C(5,12)-*rac*-Me$_6$[14]aneN$_4$·H$_2$O: C, 63.6; H, 12.6; N, 18.5. Found: C, 63.6; H, 12.7; N, 18.3. Calcd for C(5,12)-*ms*-Me$_6$[14]aneN$_4$·2H$_2$O: C, 60.0; H, 12.5; N, 17.5. Found: C, 60.2; H, 12.5; N, 17.4. Calcd for 2,3,2-tet: C, 52.5; H, 12.6; N, 35.0. Found: C, 52.4; H, 12.5; N, 34.7.

Carbonate-free sodium hydroxide stock solutions were prepared from a saturated NaOH solution and diluted with freshly distilled, deionized water. Sodium cyanide was obtained as reagent grade and used without further purification. Cyanide stock solutions were standardized by an argentimetric method[14] no more than 24 hr prior to use.

Measurements. Equilibrium measurements were obtained using a Cary 14 spectrophotometer thermostated to ±0.1°. Equilibrium was approached from both directions ensuring that the equilibrium condition was truly attained. Large excesses of both sodium cyanide and free ligand were added to either the macrocyclic complex or Ni(CN)$_4{}^{2-}$ (except for C(5,12)-*rac*-Me$_6$[14]aneN$_4$ where this is not possible because of the smaller stability constant). Equilibrium solutions were prepared using 0.1 *M* NaOH as the ionic medium. This has the effect of minimizing the concentrations of protonated ligand species (log K_1 = 11.49 for [14]aneN$_4$,[15] log K_1 = 11.69 for C(5,12)-*ms*-Me$_2$[14]aneN$_4$,[15] and log K_1 = 11.6 for C(5,12)-*rac*-Me$_6$[14]aneN$_4$[2]). All reagent solutions were flushed with nitrogen as a precaution against macrocyclic complex oxidation and decomposition of cyanide. Cyanide solutions at 2.0 × 10^{-3} *M* and 2.0 × 10^{-4} *M* showed no signs of decomposition after 3 weeks at 25.0° in 0.1 *M* sodium hydroxide. This period of time approximates that necessary for equilibration. Less than 8% decomposition occurred in a 0.1 *M* stock solution of sodium cyanide (no added hydroxide) after 100 days.[16] Equilibration of the cyanide–macrocycle solutions occurred in capped 100-ml Teflon bottles which in turn were placed in 8-oz wide-mouth bottles, capped, taped securely, and submerged in a constant-temperature water bath. The period of time for equilibration was 11 days at 40°, 14 days at 25°, and 53 days at 10° for Ni([14]aneN$_4$)$^{2+}$; 14 days at 40°, 22 days at 25°, and 117 days at 10° for Ni(C(5,12)-*ms*-Me$_2$[14]aneN$_4$)$^{2+}$; and 59 days at 25° for Ni(C(5,12)-*rac*-Me$_6$[14]aneN$_4$)$^{2+}$. Confirmation that equilibrium had indeed been obtained was indicated by checking the absorbance at several time intervals and by the convergence of the calculated equilibrium constants.

The concentration of Ni(CN)$_4{}^{2-}$ was measured from the absorbance (A) at 267 nm where $\epsilon_{Ni(CN)_4}$ is 1.16 × 10^4 M^{-1} cm^{-1} and the molar absorptivities of NiL^{2+}, NiLCN$^+$, and NiLOH$^+$ are small. In eq 2 $A_f = b\epsilon_{Ni(CN)_4}[Ni^{II}]_{total}$ and $A_i = b\epsilon_{NiL(av)}[Ni^{II}]_{total}$

$$[Ni(CN)_4{}^{2-}] = \frac{A - A_i}{A_f - A_i}[Ni^{II}]_{total} \qquad (2)$$

where $\epsilon_{NiL(av)}$ is the molar absorptivity of the mixture of NiL^{2+}, NiLCN$^+$, and NiLOH$^+$. Typical conditions caused the primary equilibrium to be that given in eq 3 where CN$^-$ and L were both present

$$NiLCN^+ + 3CN^- \rightleftarrows Ni(CN)_4{}^{2-} + L \qquad (3)$$

in much larger concentrations than either nickel species. The de-

---

[14] I. M. Kolthoff and E. B. Sandell, "Textbook of Quantitative Inorganic Analysis," Macmillan Co., New York, N. Y., 1936, p 545.

[15] A. G. McFarland and D. W. Margerum, unpublished results.

[16] G. B. Kolski, Ph.D. Thesis, Purdue University, West Lafayette, Ind., 1969, p 4.

Table I. Measured Stability Constants of [14]aneN$_4$Ni^{II} at 10, 25, and 40° and $\mu = 0.1\ M$ (NaOH)

			log K_{NiL}		
$10^5[Ni(II)]_T, M$	$10^3[CN]_T, M$	$10^3[L]_T, M$	10.0°	25.0°	40.0°
3.15[a]	2.00	1.03	23.18	21.94	20.80
3.96[b]	2.52	1.00	23.35	22.16	21.20
3.15[a]	3.00	1.03	23.37	22.12	21.02
3.96[b]	3.52	1.00	23.48	22.27	21.28
3.15[a]	4.00	1.03	23.45	22.18	21.18
3.96[b]	4.52	1.00	23.59	22.35	21.22
3.15[a]	5.00	1.03	23.59	22.31	21.29
3.96[b]	5.52	1.00	23.66	22.43	21.36
		Av	23.46 ± 0.16	22.22 ± 0.15	21.17 ± 0.18

[a] Starting with NiL^{2+}. [b] Starting with Ni(CN)$_4{}^{2-}$.

sired equilibrium constant for the formation of NiL is given by eq 4

$$K_{NiL} = \frac{[NiLCN^+]}{[Ni(CN)_4{}^{2-}]}\,\frac{[CN^-]^3}{[L]}\,\frac{\beta_4}{K_{NiLCN}} \qquad (4)$$

where β_4 is the cumulative stability constant for Ni(CN)$_4{}^{2-}$ and K_{NiLCN} is the monocyanide adduct stability constant. The determination of the monohydroxide and monocyanide adducts of the NiL^{2+} species are reported elsewhere.[17] The concentrations of NiL^{2+}, NiLOH$^+$, and NiLCN$^+$ were calculated using the measured constants and the COMICS computer program[18] in order to refine the calculated K_{NiL} values.

Calorimetric measurements were made on the unit designated CS-1 which was prepared by L. R. Morss and J. W. Cobble; a detailed description will appear elsewhere.[19] Briefly, the calorimeter consists of a standard wide-mouth 1-pt dewar flask clamped by an acrylic plastic plate onto the stirring, heating, and sensing mechanisms. The metal parts of the calorimeter were stainless steel and Teflon-coated. The stirring shaft serves as the place where the sample bulb, containing one reactant, was fastened prior to breaking. A solution of the other reactant was contained in the dewar at a volume of 530 ml. The heating element consisted of two pairs of precision resistors, each pair wired in series and the two sets wired in parellel. Two thermistors in the calorimeter assembly were connected to a Wheatstone bridge. The change in the resistance required to balance the bridge was the means of monitoring the temperature change of the calorimeter. The measurement of the heat of a reaction was made by determining the electrical equivalent of the calorimeter. The temperature of the apparatus was controlled by submerging it in a large water bath constructed from a 55-gal drum and insulated with vermiculite. The temperature was regulated by a precision temperature control unit consisting of a Sargent Model ST Thermonitor unit and a Sargent Model S-84890 Water Bath Cooler; the estimated precision was ±0.001°. The absolute temperature of the bath was determined using a platinum resistance thermometer and a Mueller bridge. The resistance developed was compared to that of an air-saturated ice-water reference. The bath temperature measured was 25.012°. This was taken as the temperature of the calorimetric experiment. The procedure followed is essentially that described by Readnour.[20] The reliability of the calorimetric apparatus and procedure were checked by measuring the heat of reaction between tris(hydroxymethylamino)methane and hydrochloric acid. The measured enthalpy is −29.694 ± 0.033 kJ/mol which is in satisfactory agreement with the reported value of −29.744 ± 0.003 kJ/mol.[21] The heat of solution of [Ni(2,3,2-tet)](ClO$_4$)$_2$ was measured in 0.11 *M* NaNO$_3$. The heat of reaction of [Ni(2,3,2-tet)](ClO$_4$)$_2$ was measured in 0.1 *M* NaOH and a 5–10% excess of cyanide ion over that needed to convert the complex to Ni(CN)$_4{}^{2-}$.

Table II. Equilibrium Data Used to Determine K_{NiL} Values and to Evaluate $\Delta H°$ and $\Delta S°$ for the Formation of Ni([14]aneN$_4$)$^{2+}$ and Ni(C(5,12)-*ms*-Me$_2$[14]aneN$_4$)$^{2+}$ at $\mu = 0.1\ M$ (NaOH)

Constant	10°	25°	40°
log $\beta_{4Ni(CN)_4}$	32.2	30.5	29.0
		L = [14]aneN$_4$	
log K_{NiLCN}	4.42	4.26	4.08
log K_{NiLOH}	0.85	0.76	0.68
log K_{NiL}	23.5 ± 0.2	22.2 ± 0.2	21.2 ± 0.2
$\Delta H° = -31.0 \pm 0.6$ kcal/mol		$\Delta S° = -2 \pm 2$ cal/(deg mol)	
		L = C(5,12)-*ms*-Me$_2$[14]aneN$_4$	
log K_{NiLCN}	4.26	4.11	4.00
log K_{NiLOH}	1.28	1.11	0.95
log K_{NiL}	23.1 ± 0.1	21.9 ± 0.1	21.02 ± 0.06
$\Delta H° = -28 \pm 1$ kcal/mol		$\Delta S° = 8 \pm 5$ cal/(deg mol)	
		L = C(5,12)-*rac*-Me$_6$[14]aneN$_4$	
log K_{NiLCN}		2.15	
log K_{NiLOH}		0.90	
log K_{NiL}		18.2 ± 0.3	

Results

[14]aneN$_4$Ni^{II}. The reaction of cyanide ion to release Ni(II) from this complex is much too slow for calorimetric studies. Although the sluggishness of the reaction makes it inconvenient to measure the equilibrium position of the reaction as a function of cyanide ion concentration and temperature, it is possible to do so and these measurements were taken spectrophotometrically over a period of 11–53 days. On the other hand the sluggishness of the NiL^{2+} dissociation reaction has the advantage of permitting the stability constants of NiLOH$^+$ and of NiLCN$^+$ to be measured in separate experiments because these species form rapidly. Table I summarizes the conditions used and the K_{NiL} values found for 10.0, 25.0, and 40.0°. A 2-cm cell path was used for the absorbance measurements at 267 nm which ranged from 0.1 to 0.7 absorbance unit for the various solutions. There is a slight trend in the values for log K_{NiL} as the CN$^-$ concentration increases, but it is within the experimental error of the results and is independent of whether the starting reactant was NiL^{2+} or Ni(CN)$_4{}^{2-}$. Table II gives the values of K_{NiLCN}, K_{NiLOH}, and β_4 used in determining K_{NiL} at each temperature. The stability constant for the NiL(CN)$_2$ complex is small[17] and the contribution from this complex is not significant. The value of log β_4 is 30.5 at 25.0° ($\mu = 0.1\ M$)[4] and the values at the other temperatures were calculated from $\Delta H° = -43.58$ kcal/mol ($\mu = 0.1\ M$).[3] The results show a very large stability constant for [14]aneN$_4$Ni^{II} with log K_{NiL} equal to 22.2 at 25°. The temperature studies indicate that the large stability constant is almost entirely due to the very negative $\Delta H°$ value of −31.0 kcal/mol for the formation of this complex from aquonickel ion and the free ligand. The $\Delta S°$ value is close to zero.

C(5,12)-*ms*-Me$_2$[14]aneN$_4$Ni^{II}. The equilibration of this complex with CN$^-$ was carried out in the same manner as with [14]aneN$_4$Ni^{II}. The conditions for the stability constant measurements are given in Table III and the results are very similar except that slightly smaller values are found for K_{NiL}. The other pertinent constants and their temperature

---

(17) F. P. Hinz and D. W. Margerum, to be submitted for publication.

(18) D. D. Perrin and I. G. Sayce, *Talanta*, **14**, 833 (1967).

(19) L. R. Morss and J. W. Cobble, to be submitted for publication.

(20) J. M. Readnour, Ph.D. Thesis, Purdue University, West Lafayette, Ind., 1969, p 10.

(21) J. O. Hill, G. Ojelund, and I. Wadso, *J. Chem. Thermodyn.*, **1**, 111 (1969).

Table III. Stability Constants of C(5,12)-*ms*-Me_2[14]aneN_4Ni^{II} at 10, 25, and 40° and $\mu = 0.1\ M$ (NaOH)

$10^5[Ni(II)]_T, M$	$10^3[CN]_T, M$	$10^3[L]_T, M$	log K_{NiL} 10.0°	25.0°	40.0°
4.09[a]	1.50	1.04	22.84	21.68	20.97
3.92[b]	2.02	1.00	22.97	21.81	20.97
4.09[a]	2.50	1.04	22.99	21.82	20.95
3.93[b]	3.02	1.00	23.07	21.91	21.01
4.09[a]	3.50	1.04	23.09	21.91	20.98
3.93[b]	4.02	1.00	23.17	22.02	21.05
4.09[a]	4.50	1.04	23.15	21.97	21.07
3.93[b]	5.02	1.00	23.22	22.09	21.13
			Av 23.06 ± 0.12	21.90 ± 0.13	21.02 ± 0.06

[a] Starting with NiL^{2+}. [b] Starting with $Ni(CN)_4^{2-}$.

Table IV. Measured Stability Constants of C(5,12)-*rac*-Me_6[14]aneN_4Ni^{II} at 25.0° and $\mu = 0.1\ M$ (NaOH)

$10^5[Ni(II)]_T, M$	$10^4[CN]_T, M$	$10^3[L]_T, M$	log K_{NiL}
1.00[a]	1.40	1.00	17.87
1.00[b]	1.90	1.00	17.96
1.00[b]	2.40	1.00	18.23
1.00[b]	3.40	1.00	18.48
		Av	18.2 ± 0.3

[a] Starting with $Ni(CN)_4^{2-}$. [b] Starting with NiL^{2+}.

Table V. Calorimetric Data for the Heat of Solution of [Ni(2,3,2-tet)]$(ClO_4)_2$ and Its Heat of Reaction with Cyanide Ion at 25°

Heat of Solution in 0.11 M $NaNO_3$ (530 ml)

Amt of [Ni(2,3,2-tet)]-$(ClO_4)_2$, g	$\Delta H°$, kcal/mol
0.25022	9.436
0.32622	9.510
0.40819	9.461
	Av 9.47 ± 0.04

Heat of Reaction with Cyanide Ion in 0.1 M NaOH (530 ml)

Amt of [Ni-(2,3,2-tet)]-$(ClO_4)_2$, g	$[CN^-], M$	$\Delta H°$, kcal/mol
0.24467	6.00×10^{-3}	−14.76
0.43202	9.00×10^{-3}	−14.76
0.50861	1.05×10^{-2}	−14.64
0.60645	1.43×10^{-2}	−14.86
		Av −14.76 ± 0.09

dependence which lead to a $\Delta H°$ value of −28 kcal/mol are given in Table II. In this case the $\Delta S°$ value is positive but the experimental error is greater than for [14]aneN_4Ni^{II}.

C(5,12)-*rac*-Me_6[14]aneN_4Ni^{II}. The stability constant of this complex is significantly lower than for the [14]aneN_4 or Me_2[14]aneN_4 complexes and therefore lower CN^- concentrations were necessary in order to establish an equilibrium mixture with $Ni(CN)_4^{2-}$. The monocyanide adduct constant also is weaker (Table II) and as a result the primary species at equilibrium are NiL^{2+} and $Ni(CN)_4^{2-}$. This was taken into account in the calculations for K_{NiL} and the computation adjusted for the mixture of NiL^{2+}, $NiLCN^+$, and $NiLOH^+$ species which were present at each condition given in Table IV. The reaction mixture was slow to reach equilibrium, requiring 2 months at 25°. At low CN^- concentrations there were some problems due to slight decomposition of the macrocyclic ligand over the long periods needed for equilibration. Hence, stability constants were determined only at 25° and the constants are not as precise as those for the [14]aneN_4 and Me_2[14]aneN_4. Nevertheless, the accuracy is sufficient to conclude that the six methyl groups in C(5,12)-*rac*-Me_6[14]aneN_4 cause the stability constant for the nickel complex to be smaller by a factor of 10^4.

C(5,12)-*ms*-Me_6[14]aneN_4Ni^{II}. An accurate value of the stability constant for Ni(C(5,12)-*ms*-Me_6[14]ane$N_4)^{2+}$ could not be obtained by the same procedure because of the limitted solubility of the free ligand. In those experiments where the cyanide ion concentration was very low, equilibrium constants could be calculated. The values averaged 1 log unit greater than the stability constant calculated for the *rac*-Me_6 derivative. However, on the basis of the observed values of A_∞ in kinetic measurements of CN^- attack, the log K_{NiL} value was estimated to be 21. Therefore the complex Ni(C(5,12)-*ms*-Me_6[14]ane$N_4)^{2+}$ is assigned a stability constant of log $K_{NiL} \simeq 20 \pm 1$.

2,3,2-tetNi^{II}. There are several reasons why it is difficult to determine the stability constants and enthalpy of formation of Ni(2,3,2-tet$)^{2+}$ by the cyanide ion equilibration method used with the macrocyclic ligands. The K_{NiL} value is much smaller and therefore high concentrations of 2,3,2-tet would be needed, but this causes the bis complex Ni(2,3,2-tet$)_2^{2+}$ to form. The stoichiometry and stability constants of mixed cyanide and 2,3,2-tet complexes of nickel are not known and are difficult to determine because of the rapid formation of $Ni(CN)_4^{2-}$. On the other hand, the lability of the cyanide ion reaction permits calorimetric procedures to be used and the K_{NiL} value has already been measured at 25° by potentiometric titration.[22] The use of the cyanide ion reaction rather than additional potentiometric studies at several temperatures eliminates the necessity of measuring all the protonation constants and provides a basis for comparison with the macrocyclic ligands.

The heat of formation of $Ni(CN)_4^{2-}$ from Ni(2,3,2-tet$)^{2+}$, −24.23 kcal/mol, was obtained by combining the heat of solution of solid [Ni(2,3,2-tet)]$(ClO_4)_2$ (eq 5) in 0.11 M

$$[\mathrm{Ni(2,3,2\text{-}tet)}](\mathrm{ClO_4})_2(s) \rightarrow \mathrm{Ni(2,3,2\text{-}tet)}^{2+}(aq) + 2\mathrm{ClO_4}^-(aq) \quad (5)$$

$NaNO_3$ with the heat of reaction with cyanide ion (eq 6) in

$$[\mathrm{Ni(2,3,2\text{-}tet)}](\mathrm{ClO_4})_2(s) + 4\mathrm{CN}^-(aq) \rightarrow \mathrm{Ni(CN)_4}^{2-}(aq) + \mathrm{2,3,2\text{-}tet}(aq) + 2\mathrm{ClO_4}^- \quad (6)$$

0.1 M NaOH (Table V). The $NaNO_3$ was used in the determination of the heat of solution instead of NaOH to avoid precipitation of $Ni(OH)_2$, log $K_{so} = -14.7$[23]. The choice of $NaNO_3$ as a substitute for NaOH was made because of the similarity of its mean activity coefficient with that of NaOH [0.762 for $NaNO_3$[24] *vs.* 0.766 for NaOH[25] at $\mu = 0.1\ M$]. It was desirable to use NaOH as the ionic strength control for

---

(22) D. C. Weatherburn, E. J. Billo, J. P. Jones, and D. W. Margerum, *Inorg. Chem.*, 9, 1557 (1970).

(23) W. Feitknecht and P. Schindler, *Pure Appl. Chem.*, 6, 130 (1963).

(24) R. A. Robinson, *J. Amer. Chem. Soc.*, 57, 1165 (1935).

(25) B. E. Conway, "Electrochemical Data," Elsevier, Amsterdam, 1952, p 76.

comparison with the thermodynamic parameters of the macrocyclic complexes which were evaluated in that medium. Since log K_1 is 10.25 for the first protonation of 2,3,2-tet,[22] protonated species are not important under these conditions. Adding the heat of formation of Ni(2,3,2-tet) from $Ni(CN)_4^{2-}$ (eq 7) and the heat of formation of $Ni(CN)_4^{2-}$ (eq 8, where

$$Ni(CN)_4^{2-}(aq) + 2,3,2\text{-tet}(aq) \rightarrow Ni(2,3,2\text{-tet})^{2+}(aq) + 4CN^-(aq) \quad (7)$$

$$Ni^{2+}(aq) + 4CN^-(aq) \rightarrow Ni(CN)_4^{2-}(aq) \quad (8)$$

a $\Delta H°$ value of −43.58 kcal/mol is calculated by interpolation of the experimental values at $\mu = 0.082$ and $\mu = 0.134$)[3] gives the heat of formation of $Ni(2,3,2\text{-tet})^{2+}(aq)$ as −19.4 kcal/mol (eq 9).

$$Ni^{2+}(aq) + 2,3,2\text{-tet}(aq) \rightarrow Ni(2,3,2\text{-tet})^{2+}(aq) \quad (9)$$

Discussion

Stability Constants of the Macrocyclic Complexes. The macrocyclic ligand [14]aneN_4 forms a nickel(II) complex with a stability constant more than 10^6 times greater than that for $Ni(2,3,2\text{-tet})^{2+}$. The constants are summarized in Table VI where the 2,3,2-tet constant has been corrected from its value of $10^{16.4}$ at $\mu = 0.5$ *M* to a value of $10^{15.8}$ at $\mu = 0.1$ *M* by assuming that the same correction applies as that found for $Ni(trien)^{2+}$ [where log K_{NiL} is 14.4 at 0.5 *M* KCl and is 13.8 at 0.1 *M* KCl[26]]. The presence of methyl substituents to the 14-membered macrocyclic ring tends to have a destabilizing influence. The effect is small with only two methyl groups but is significant with six methyl groups. The *ms*-Me_6 complex is believed to have the same arrangement of its chelate rings[27] as the [14]aneN_4Ni^{II} complex[28] and the Me_2-[14]aneN_4Ni^{II} complex is assumed to be similar. The decrease in the K_{NiL} value by approximately 2 orders of magnitude for the *rac*-Me_6 complex compared to the *ms*-Me_6 complex can be attributed in part to interference of the methyl groups with axial solvation of the nickel.[27] In addition, the presence of six methyl groups may cause increased tetrahedral distortion of the four nitrogen donor atoms from planarity. A similar distortion has been observed for [Ni-(C(3,10)-*rac*-Me_8[14]-4,11-dieneN_4)]$(ClO_4)_2$[29] compared to [Ni(Me_6[14]-4,11-dieneN_4)]$(ClO_4)_2$,[30] although the chelate ring conformations remain the same. A distortion of this type could cause a reduction in the Ni–N bond strengths. The ring conformations of the *rac*-Me_6 complex are known[31] and are thought to be less favorable than those in the *ms*-Me_6 complex. Whimp, Bailey, and Curtis[32] estimated that the chelate ring conformations in the *rac*-Me_6 complex would cause it to be 4 kcal/mol less stable than the *ms*-Me_6 complex. Our results indicate that the *rac*-Me_6 complex is 2 kcal/mol less favorable in overall stability than the *ms*-Me_6 complex.

Table VI. Stability Constants of Tetramine Complexes at 25.0° and $\mu = 0.1$

Complex	Other common abbrev for cyclic ligands	log K_{NiL}
[14]aneN_4Ni^{II}	Cyclam	22.2
C(5,12)-*ms*-Me_2[14]aneN_4Ni^{II}	Me_2cyclam	21.9
C(5,12)-*ms*-Me_6[14]aneN_4Ni^{II}	tet *a*	~20
C(5,12)-*rac*-Me_6[14]aneN_4Ni^{II}	tet *b*	18.2
(2,3,2-tet)Ni^{II}		15.8

Table VII. Stability Constants, Enthalpy, and Entropy of Formation of the Nickel Complexes of Tetramines at 25.0° and $\mu = 0.1$

Complex	log K_{NiL}	$\Delta H°$, kcal/mol	$\Delta S°$, cal/(deg mol)
$Ni(trien)^{2+}$ [a]	13.8	−14.0	16.0
$Ni(2,3,2\text{-tet})^{2+}$	15.8[b]	−19.4	7.2
$Ni(C(5,12)\text{-}ms\text{-}Me_2[14]aneN_4)^{2+}$	21.9	−28	8
$Ni([14]aneN_4)^{2+}$	22.2	−31	−2
$Ni(2,3,2\text{-tet})^{2+}$(sp)[c]	15.3	−16.8	13.8
$Ni(trien)^{2+}$(sp)[c]	11.9	−10.6	18.7

[a] Reference 26, 0.1 *M* KCl. [b] log K_{NiL} is 16.4 in 0.5 *M* KCl and is corrected to $\mu = 0.1$ assuming the same ionic strength dependence as found for $Ni(trien)^{2+}$ from ref 22 and 26. [c] $\Delta H°$ and $\Delta S°$ are corrected to complete formation of the square-planar coordination geometry of the complex using log *K*, $\Delta H°$, and $\Delta S°$ data for the blue, octahedral to yellow, square-planar equilibrium: D. C. Weatherburn and D. W. Margerum, unpublished data. sp = square planar.

The stability constant of the copper complex of C(5,12)-*ms*-Me_6[14]aneN_4 which was measured by Cabbiness and Margerum[1] gave a log K_{CuL} value of 28 at $\mu = 0.1$ *M*, 25°. A comparison of the relative stability constants of five different tetramine (2,3,2-tet, trien, 3,3,3-tet, $(en)_2$, $(pn)_2$) complexes of Cu(II) and of Ni(II) indicates that the average Δ log K_{ML} (=log K_{CuL} − log K_{NiL}) is 6.7 log units.[33] Therefore, the difference of eight orders of magnitude for the copper and nickel constants with the *ms*-Me_6 ligand is not unreasonable and agrees very well with a Δ log K_{ML} value of 7.5 for the open-chain ligand with a similar sequence of 5,6,5-membered rings (*i.e.*, 2,3,2-tet). It also is possible to predict that the log K_{CuL} for [14]aneN_4Cu^{II} should be equal to 30 ± 1, on the assumption that the six methyl substituents will have a similar effect on the stabilities of the copper and nickel complexes.

Thermodynamic Constants of Square-Planar Nickel(II)-Tetramine Complexes. A comparison of the $\Delta H°$ and $\Delta S°$ values in Table VII shows that the enhanced stability of the macrocyclic complex is due primarily to the enthalpic contribution for both [14]aneN_4 and its dimethyl derivative.

The conditions under which calorimetric measurement of $\Delta H°$ for $Ni(2,3,2\text{-tet})^{2+}$ was obtained were chosen to afford the greatest similarity to those conditions under which the experiments on the macrocyclic complexes were performed. Therefore the heat of the cyanide displacement of 2,3,2-tet from the nickel ion was determined and combined with the heat of formation of $Ni(CN)_4^{2-}$ to obtain the heat of formation of $Ni(2,3,2\text{-tet})^{2+}$. Subsequent to this experiment, the heat of formation of $Ni(2,3,2\text{-tet})^{2+}$ was reported in the literature.[34] The value of −17.9 kcal/mol was obtained by the reaction between the nickel complex and excess HCl in 0.5 *M* KCl and differs appreciably from the value −19.4 kcal/mol obtained by our cyanide displacement data. Both

---

(26) L. Sacconi, P. Paoletti, and M. Ciampolini, *J. Chem. Soc.*, 5115 (1961).

(27) L. G. Warner and D. H. Busch, *J. Amer. Chem. Soc.*, 91, 4092 (1969).

(28) B. Bosnich, R. Mason, P. J. Pauling, G. B. Robertson, and M. L. Tobe, *Chem. Commun.*, 97 (1965).

(29) D. W. Swann, T. N. Waters, and N. F. Curtis, *J. Chem. Soc., Dalton Trans.*, 1115 (1972).

(30) M. F. Bailey and I. E. Maxwell, *J. Chem. Soc., Dalton Trans.*, 938 (1972).

(31) N. F. Curtis, D. A. Swann, and T. N. Waters, *J. Chem. Soc., Dalton Trans.*, 1963 (1973).

(32) P. O. Whimp, M. F. Bailey, and N. F. Curtis, *J. Chem. Soc. A*, 1956 (1970).

(33) Reference 22, 2,3,2-tet; ref 26, trien; R. Barbucci, L. Fabbrizzi, and P. Paoletti, *J. Chem. Soc., Dalton Trans.*, 745 (1972), 3,3,3-tet; T. Davies, S. S. Singer, and L. A. K. Staveley, *J. Chem. Soc.*, 2304 (1954), bis(ethylenediamine); I. Poulsen and J. Bjerrum, *Acta Chem. Scand.*, 9, 1407 (1955), propylenediamine.

(34) L. Fabbrizzi, R. Barbucci, and P. Paoletti, *J. Chem. Soc., Dalton Trans.*, 1529 (1972).

experiments required the inclusion of independently measured constants. Decomposition by cyanide requires only the value of $\Delta H°$ for the formation of $Ni(CN)_4^{2-}$ to calculate the heat of formation of $Ni(2,3,2\text{-tet})^{2+}$. On the other hand, the calculation of $\Delta H°$ for the formation of $Ni(2,3,2\text{-tet})^{2+}$ by acid decomposition involved six independently measured constants (the four successive protonations of the free ligand, the stability constant of $Ni(2,3,2\text{-tet})^{2+}$, and the stability constant of $Ni(2,3,2\text{-tet})_2^{2+}$). These constants were used to calculate the concentration of the species before and after the reaction enabling extraction of $\Delta H°$ for $Ni(2,3,2\text{-tet})^{2+}$ and $Ni(2,3,2\text{-tet})_2^{2+}$ from the experimental heat of reaction by successive approximation. The values of $\Delta H°$ for the stepwise protonations were previously measured by a calorimetric titration making use of the four protonation constants to calculate the species distribution before and after complete reaction. It was necessary to solve for the $\Delta H°$ values of the four protonations by successive approximation and to correct the experimentally measured heat of reaction. It would appear that decomposition of $Ni(2,3,2\text{-tet})^{2+}$ by cyanide is a more direct (or, better stated, less indirect) method for evaluating the heat of formation of $Ni(2,3,2\text{-tet})^{2+}$ than is decomposition by acid. It is preferred in the present study for comparison to the thermodynamic parameters of the macrocyclic complexes because of the similarities in the experimental conditions under which each was evaluated. However, the major conclusions drawn from the comparison with macrocyclic complex constants are not affected by the choice of $\Delta H°$ (or $\Delta S°$).

The $Ni([14]aneN_4)^{2+}$ complex is yellow in aqueous solution and has the spectral characteristics of a square-planar nickel complex without appreciable contribution from the blue diaquo octahedral derivative which exists in equilibrium with yellow complexes of $Ni(2,3,2\text{-tet})^{2+}$ and $Ni(trien)^{2+}$. It is desirable to correct the $\Delta H°$ and $\Delta S°$ values of the latter complexes so that specific comparison can be made for the formation of the square-planar (sp) complexes. This is possible because there have been temperature studies of the equilibrium in eq 10 for both trien and 2,3,2-tet.[35] The

$$NiL(H_2O)_2^{2+}(\text{blue, oct}) \rightleftarrows NiL^{2+}(\text{yellow, sp}) + 2H_2O \qquad (10)$$

enthalpy change of eq 10 was found to be 3.3 ± 0.4 kcal/mol for $Ni(2,3,2\text{-tet})^{2+}$ and 3.4 ± 0.4 kcal/mol for $Ni(trien)^{2+}$. The ionic strength medium for the 2,3,2-tet data was varied between 0.54 and 4.5 M $NaClO_4$. The ionic strength range for the trien data was 0.54 to 1.80 M $NaClO_4$. Extrapolating the equilibrium data reported to 0.1 M ionic strength gave an equilibrium constant for the blue-to-yellow conversion of 0.28 for $Ni(2,3,2\text{-tet})^{2+}$ and 0.012 for $Ni(trien)^{2+}$. The equilibrium data allow the calculation of the entropy of the blue-to-yellow conversion at 0.1 M ionic strength. The entropy values are 8.5 and 2.7 cal/(deg mol) for $Ni(2,3,2\text{-tet})^{2+}$ and $Ni(trien)^{2+}$, respectively. The values of $\Delta S°$ for eq 10 when L is 2,3,2-tet or trien are small when compared to the estimated value of $\Delta S° = 7.3$ cal/(deg mol) for the liberation of a single coordinated water molecule. The latter value was obtained by subtracting the entropy contribution of a single molecule of water of hydration in a solid compound, 9.4 cal/(deg mol),[36] from the entropy of liquid water, 16.71 cal/(deg mol).[37] The $\Delta S°$ value for the breaking of a hydrogen bond and releasing a water molecule is 2–3 times greater than found for eq 10 ($\Delta H°$ and $\Delta S°$ for hydrogen bonds are discussed later). The larger values of $\Delta S°$ expected for the complete liberation of a coordinated water molecule suggest that the yellow, square-planar complex of the right-hand side of eq 10 is not devoid of axial solvation but might be more correctly considered as an extremely tetragonally distorted octahedral complex. [However, $Ni(trien)(H_2O)_2^{2+}$ may be cis octahedral[22] so that its $\Delta S°$ value could also reflect a change in configuration of the ligand.] The Ni(II) complex of $[14]aneN_4$ is almost entirely square planar while $Ni(trien)^{2+}$ is almost entirely octahedral with two coordinated water molecules; $Ni(2,3,2\text{-tet})^{2+}$ is intermediate between the two situations. Therefore the square-planar geometry was chosen to compare the thermodynamic terms of these systems. Since 99% of the $Ni(trien)^{2+}$ exists as the blue, octahedral species, the thermodynamic parameters for the octahedral to square-planar equilibrium may simply be added to the thermodynamic data for the formation reaction. Within experimental error, $Ni([14]aneN_4)^{2+}$ is all in the square-planar form so no correction to the formation data is necessary. The equilibrium for $Ni(2,3,2\text{-tet})^{2+}$ is intermediate with 22% present as the square-planar form and 78% present as the octahedral form at 25°, $\mu = 0.1$ M. Therefore 78% of the enthalpy and entropy of the octahedral to square-planar reaction (eq 10) must be added to the formation enthalpy and entropy for $Ni(2,3,2\text{-tet})^{2+}$. The data for the reaction, depicted by eq 11, are given in Table VII at $\mu = 0.1$ and 25° along with the

$$Ni^{2+}(aq) + L(aq) \rightarrow NiL^{2+}(sp) \qquad (11)$$

experimental values.

Comparing $\Delta H°$ for $Ni([14]aneN_4)^{2+}$ and $Ni(2,3,2\text{-tet})^{2+}(sp)$ shows the formation of the cyclic complex to be more enthalpic by 14 kcal/mol. An enhancement of the nickel-nitrogen bond strengths could not possibly account for the 14-kcal/mol difference between the $\Delta H°$ values for $Ni(2,3,2\text{-tet})^{2+}$ and $Ni([14]aneN_4)^{2+}$. Although secondary amines have greater Bronsted base strengths than primary amines, steric crowding is more serious with metal ions and the net effect is that primary amines usually form stronger metal complexes. However, $\Delta H° = -25.4$ kcal/mol for the formation of $Cu(en)_2^{2+}$ in 1.0 M KNO_3[33] while $\Delta H° = -27.7$ kcal/mol for the formation of $Cu(2,3,2\text{-tet})^{2+}$ in 0.5 M KCl.[33] The 2-kcal/mol difference might be due to a combination of steric and inductive effects. A similar situation occurs with $Ni(2,3,2\text{-tet})^{2+}$ and $Ni(en)_2^{2+}$ where the difference is 1–2 kcal/mol.[38] Since the difference between a $(en)_2$ complex and a 2,3,2-tet complex is in the formation of a six-membered chelate ring and the conversion of two primary amine nitrogens to secondary amine nitrogens, a difference of at most 2 kcal/mol would be expected between the heat of formation of $Ni(2,3,2\text{-tet})^{2+}$ and $Ni([14]aneN_4)^{2+}$ due to bond strength. It is interesting that approximately 2 kcal/mol was estimated to be the difference in $\Delta H°$ for $Cu(2,3,2\text{-tet})^{2+}$ and $Cu(C(5,12)\text{-}ms\text{-}Me_6[14]aneN_4)^{2+}$, from a correlation between $\Delta H°$ and λ_{max}.[39] However, 2 kcal/mol is far short of the difference of 14 kcal/mol found in the $\Delta H°$ values of $Ni(2,3,2\text{-tet})^{2+}(sp)$ and $Ni([14]aneN_4)^{2+}$.

The influence of chelate ring size and conformation on the magnitude of $\Delta H°$ can be seen by comparing the values for $Ni(trien)^{2+}(sp)$ and $Ni(2,3,2\text{-tet})^{2+}(sp)$ in Table VII. The

---

(35) D. C. Weatherburn and D. W. Margerum, unpublished data.

(36) W. M. Latimer, "Oxidation Potentials," 2nd ed, Prentice-Hall, Englewood Cliffs, N. J., 1952, p 364.

(37) *Nat. Bur. Stand. (U. S.), Tech. Note*, No. 270-3, 13 (1968).

(38) S. J. Ashcroft and C. T. Mortimer, "Thermochemistry of Transition Metal Complexes," Academic Press, London, 1970, p 25.

(39) P. Paoletti, L. Fabbrizzi, and R. Barbucci, *Inorg. Chem.*, 12, 1961 (1973).

6-kcal/mol difference stems from the inability of the middle ethylene linkage of trien to span effectively the square-planar sites as shown in the crystal structure of the square-planar $Ni(trien)(ClO_4)_2$ complex.[40] As a result the Ni–N bonding is slightly trapezoidal and the middle chelate ring is in an eclipsed conformation.[40] Thus, the less favorable ΔH° can be attributed to both weaker Ni–N bonding and to less favorable ring conformation. The arrangement of 5,6,5,6-membered chelate rings is the most favorable for macrocyclic ligands as it holds cumulative ring strain to a minimum.[41] The 5,6,5-membered chelate ring arrangement also is the most favorable for the noncyclic tetramines.[22,41] Therefore, the difference in ΔH° for the 2,3,2-tet complex and for the $[14]aneN_4$ complex cannot be attributed to differences in either Ni–N bonding or to ring conformations. Restricting the flexibility of the ligand cannot force the donor atoms into a more favorable coordination geometry in the macrocycle than the donors are free to adopt in the open-chain ligand. Hence another explanation is needed to account for the large enthalpic contribution to the stability of the macrocyclic complex. One factor which has been largely overlooked in consideration of metal complex stability constants and enthalpies is the effect of ligand solvation.

Ligand Solvation and the Macrocyclic Effect. The enhanced stability of the macrocyclic tetramine ligand complex compared to its open-chain analog is due almost entirely to an enthalpic contribution. A comparison of the corrected values of ΔH° and ΔS° for $Ni([14]aneN_4)^{2+}$ and $Ni(2,3,2\text{-tet})^{2+}(sp)$ shows the macrocyclic ligand to have a more favorable ΔH° by 14 kcal/mol and a less favorable ΔS° by 16 cal/(deg mol). The noncyclic ligand would be expected to suffer a much larger loss of configurational entropy upon coordination than the cyclic ligand where the geometry is already restricted. However, the experimental ΔS° differences are in the opposite direction. Furthermore, as already discussed, no more than 2 kcal/mol could be assigned to differences in Ni–N bond strengths in the two complexes.

The relative enthalpy and entropy changes can be understood if ligand solvation is taken into consideration. The complexation reaction in aqueous solution is given by eq 12

$$Ni(H_2O)_x{}^{2+} + L(H_2O)_y \rightarrow NiL(H_2O)_2{}^{2+} + (x + y - 2)H_2O \qquad (12)$$

where the free ligand, L, is hydrated primarily through hydrogen bonding. The nickel ion has six water molecules in its inner coordination sphere and additional water molecules associated with it in the outer hydration shell. The complex will be less hydrated than the metal ion because of the ligand coordination, the decreased charge to radius ratio, and the hydrophobic exterior presented by the bound ligand. The net heat of formation of the nickel complex is equal to the enthalpy of Ni–N bond formation after correction for the configurational energy less the additional hydration enthalpy of the nickel ion and the ligand. The release of water from the metal ion and the ligand results in a positive entropy contribution because the number of independent particles has been increased, but a negative contribution to the entropy change stems from the loss of configurational entropy of the ligand upon coordination. Although the interactions of water with the metal ion are in general stronger than with the ligand, the major difference in the formation reactions of $Ni(2,3,2\text{-tet})^{2+}$ and $Ni([14]aneN_4)^{2+}$ is due to the magnitude of y in eq 12. The cyclic nature of $[14]aneN_4$ physically prevents it from having as large a hydration number as 2,3,2-tet. This is reflected in the lower solubility of the cyclic ligand (but crystal lattice forces also enter in). The effect of the proximity of the nitrogen donors to one another is seen in the protonation constants. The first and second protonation constants for $[14]aneN_4$ measured by potentiometric titration[15] are $10^{11.49}$ and $10^{10.24}$, respectively, while the values for 2,3,2-tet[22] are $10^{10.25}$ and $10^{9.50}$, respectively. Internal hydrogen bonding in the cyclic ligand can account for these differences. On the other hand the third and fourth protonation constants[15] for $[14]aneN_4$ are $10^{1.64}$ and $10^{0.86}$ compared to $10^{7.28}$ and $10^{6.02}$ for 2,3,2-tet. The big gap between the second and third protonation constants of the cyclic ligand is caused by the necessity of breaking internal hydrogen bonding of the first two protons as well as by the electrostatic repulsion due to the proximity of the donor sites to one another. [One consequence of the difference in the protonation constants is to make the conditional stability constant[42] of the cyclic complex as much as 10^{15}–10^{17} times larger than that of $Ni(2,3,2\text{-tet})^{2+}$ in acidic solutions.]

Since hydrogen bonding of the ligand to water is an important part of ligand solvation, some thermodynamic constants of hydrogen bond formation with nitrogen bases are given in Table VIII.[43-47] The average values of hydrogen bond formation are $\Delta H^\circ = -7.3$ kcal/mol and $\Delta S^\circ = -18$ cal/(deg mol). When H_2O is the solvent, the values of ΔH° and ΔS° for hydrogen bond formation should become less negative because of extensive hydrogen bonding present in bulk water. Nevertheless the heat and entropy of solvation for ammonia ($NH_3(g) \rightarrow NH_3(aq)$), $\Delta H^\circ = -8.3$ kcal/mol and $\Delta S^\circ = -19.7$ cal/(deg mol),[48] are in fair agreement with the values estimated from Table VIII. Although hydrogen-bond interactions of ammonia may involve N–H with an electron pair of the oxygen atom from water or O–H with an electron pair from the nitrogen atom of ammonia, the interaction involving the electron pair on the nitrogen atom should be the major contributor to thermodynamic constants for ammonia solvation (the calculated strength of the $H_3N\cdots HOH$ interaction is 3.5 kcal/mol stronger than the calculated strength of the $H_2O\cdots HNH_2$ interaction).[47] Comparing the average ΔH° value for the hydrogen-bond formation from Table VIII with the ΔH° values for the formation of $Ni(2,3,2\text{-tet})^{2+}(sp)$ and $Ni([14]aneN_4)^{2+}$ from Table VII indicates the cyclic ligand is solvated by the equivalent of at least two fewer water molecules. The much less favorable entropy change expected for the formation of a complex containing $[14]aneN_4$ due to the liberation of fewer water molecules (rupture of fewer hydrogen bonding interactions) upon coordination is largely offset by a smaller loss in configurational entropy (compared to a noncyclic ligand such as 2,3,2-tet). The smaller loss in configurational entropy for $[14]aneN_4$ is expected because of the cyclic nature of the ligand.

In conclusion, the dominant factor responsible for the

---

(40) A. McPherson, Jr., M. G. Rossmann, D. W. Margerum, and M. R. James, *J. Coord. Chem.*, **1**, 39 (1971).

(41) G. R. Hedwig, J. L. Love, and H. K. J. Powell, *Aust. J. Chem.*, **23**, 981 (1970).

(42) A. Ringbom, "Complexation in Analytical Chemistry," Interscience, New York, N. Y., 1963, p 35.

(43) H. Fritzsche, *Ber. Bunsenges. Phys. Chem.*, **68**, 459 (1964).

(44) E. M. Arnett, L. Joris, E. Mitchell, T. S. S. R. Murty, T. M. Gorrie, and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **92**, 2365 (1970).

(45) R. A. Hudson, R. M. Scott, and S. N. Vinogradov, *Spectrochim. Acta, Part A*, **26**, 337 (1970).

(46) A. D. H. Clague, G. Govil, and H. S. Bernstein, *Can. J. Chem.*, **47**, 625 (1969).

(47) P. A. Kollman and L. C. Allen, *J. Amer. Chem. Soc.*, **93**, 4991 (1971).

(48) Reference 36, p 91.

Table VIII. Thermodynamic Constants of Hydrogen Bond Formation

System	Medium	$\Delta H°$, kcal/mol	$\Delta S°$, cal/(deg mol)	Ref
Phenol–pyridine	CCl_4, 20°	−6.5	−14.4	43
p-Fluorophenol–pyridine	CCl_4, 25°	−7.1	−15.2	44
Phenol–triethylamine	CCl_4, 20°	−8.4	−20.0	43
p-Nitrophenol–triethylamine	C_6H_{12}, 25°	−10.2	−20.2	45
Methanol–trimethylamine	Vapor	−5.85	−22.6	46
Water–ammonia	Calcd[a]	−5.8		47

[a] Theoretical H-bond strength of the H_3N–HOH dimer.

macrocyclic effect in the tetramine ligands is the lower degree of solvation of the macrocycle. A smaller, but important contributing factor is the lower configurational entropy of the ligand because it is already cyclic. The latter factor tends to be obscured in the present data because the more solvated ligand releases additional water in its reaction and gives a larger $\Delta S°$ value.

Because the *macrocyclic effect* with the tetramine ligands has its origin in the differences of ligand hydration, the effect should be independent of metal ion as long as the coordination geometry of the macrocycle around the metal ion is not unfavorable. Thus, both Ni(II) and Cu(II) show similar enhanced stability constants with these macrocyclic ligands.

The $\Delta H°$ and $\Delta S°$ values for the formation of the nickel complex with *ms*-Me_2[14]aneN_4 also are given in Table VII and the enthalpic term is again the main reason for the enhanced stability constant. However, the presence of the two methyl groups causes $\Delta H°$ to be smaller by 3 kcal/mol and $\Delta S°$ to be larger by 10 cal/(deg mol) than for the corresponding reaction with [14]aneN_4. Steric effects of the methyl groups would be expected to build more configurational entropy into the free ligand, causing $\Delta S°$ to be larger. The less favorable $\Delta H°$ value could be due to small repulsive forces of the methyl groups for neighboring atoms in the coordinated molecule, or conversely such steric effects could cause small deviations from the optimum positioning of the donor groups around nickel.

Macrocyclic ligands which do not have strong hydrogen-bonding interaction with the solvent should show decreased $\Delta H°$ and increased $\Delta S°$ values relative to their open-chain analogs. Preliminary results in nitromethane indicate the nickel complexes of 1,4,8,11-tetrathiacyclotetradecane (the sulfur analog of [14]aneN_4) and the noncyclic thioether 2,5,9,12-tetrathiatridecane have formation constants in approximately a ratio of 100:1.[49] Because the noncyclic thioether contains all secondary sulfurs and possesses solvation properties closer to those of a cyclic ligand in nitromethane, the enhanced stability of the complex of the cyclic ligand is believed to be due to the smaller loss of configurational entropy upon coordination to the nickel ion.

The cyclic polyethers[50] show small negative $\Delta H°$ values and mostly negative $\Delta S°$ values in their complexation reactions with uni- and bivalent metal ions in aqueous solution.[51] Izatt, *et al.*, suggest that there is a near compensation of the factors which determine the magnitude of $\Delta S°$; *i.e.*, ligand conformation changes upon complexation as well as changes in ligand and metal ion hydration and changes in total number of particles. These authors also recognized the importance of ligand solvation in the behavior of different ligand isomers.

The predicted ligand solvation effects in water are not restricted to macrocyclic ligands but should hold for any ligands where hydrogen bonding donor groups are forced to be close to one another. An example is seen in a comparison of the $\Delta H°$ and $\Delta S°$ values in eq 13 and 14 where

$$Ni(NH_3)_2(H_2O)_4^{2+} + en(H_2O)_2 \rightarrow Ni(en)(H_2O)_4^{2+} + 2NH_3(H_2O)$$
$$\Delta H° = -2.4 \text{ kcal/mol}, \Delta S° = 6 \text{ cal/(deg mol)} \qquad (13)$$

$$Ni(py)_2(H_2O)_4^{2+} + phen(H_2O) + H_2O \rightarrow Ni(phen)(H_2O)_4^{2+} + 2py(H_2O)$$
$$\Delta H° = -5.8 \text{ kcal/mol}, \Delta S° = 2 \text{ cal/(deg mol)} \qquad (14)$$

the thermodynamic values are taken from the *formation* reactions of nickel with phen[52], with bis(pyridine),[53] with bis(ammonia),[54] and with ethylenediamine,[55] and the primary solvation assignments are our own. The more favorable $\Delta H°$ and less favorable $\Delta S°$ values for eq 14 compared to eq 13 suggest a behavior similar to that found for the open-chain *vs.* cyclic tetramines. The greater solvation of two free pyridine molecules compared to 1,10-phenanthroline can account for much of the $\Delta H°$ difference in eq 13 and 14 and may be more important than differences in π back-bonding between these heterocyclic ligands. There are three particles on each side of eq 14 and the rigidly constrained geometry of 1,10-phenanthroline causes relatively little loss in configurational entropy, so that the $\Delta S°$ change is very small. In eq 13 there is a gain in translational entropy which is partially offset by the loss of configurational entropy of ethylenediamine on chelation so that the net increase of $\Delta S°$ is only 6 cal/(deg mol). This interpretation suggests that if bipyridyl is used instead of 1,10-phenanthroline in eq 14, there will be a significantly smaller $\Delta H°$ change and this is indeed the case.[52,56]

The effect of solvent on the thermodynamic constants of complex formation is dramatically illustrated by the ethylenediamine complexes of the lanthanide ions in anhydrous acetonitrile.[57] While lanthanide complexes in aqueous solution exhibit small negative or slightly positive enthalpy changes and large positive entropy changes, the behavior of ethylenediamine in acetonitrile is very different. It exhibits large negative enthalpy and large negative entropy changes ($\Delta H_1° = -17.3$ kcal/mol and $\Delta S_1° = -15.1$ cal/(deg mol) for the formation of $La(en)^{3+}$ at 23°). The more favorable enthalpy change in acetonitrile is consistent with the solvent being a weaker coordinating ligand than water and with less solvation of ethylenediamine. The $\Delta S_1°$ value in acetonitrile is very negative despite the ethylenediamine displacement of coordinated acetonitrile molecules because of the loss of configurational entropy of ethylenediamine upon

---

(49) G. F. Smith and D. W. Margerum, unpublished data.

(50) C. J. Pedersen, *J. Amer. Chem. Soc.*, **89**, 7017 (1967).

(51) R. M. Izatt, D. P. Nelson, J. H. Rytting, B. L. Haymore, and J. J. Christensen, *J. Amer. Chem. Soc.*, **93**, 1619 (1971).

(52) G. Anderegg, *Helv. Chim. Acta*, **46**, 2813 (1963).

(53) G. Atkinson and J. E. Bauman, Jr., *Inorg. Chem.*, **2**, 64 (1963).

(54) J. L. Schultz, Ph.D. Thesis, University of Minnesota, Minneapolis, Minn., 1959.

(55) I. Poulsen and J. Bjerrum, *Acta Chem. Scand.*, **9**, 1407 (1955).

(56) G. Atkinson and J. E. Bauman, Jr., *Inorg. Chem.*, **1**, 900 (1962).

(57) J. H. Forsberg and T. Moeller, *Inorg. Chem.*, **8**, 889 (1969).

chelation. Reactions of ethylenediamine with metal ions in water generally have positive entropy changes because of the additional release of water that was initially hydrogen bonded to the ligand. Thus, our interpretation of these results indicates the importance of ligand solvation as well as metal ion solvation.

The effect of ligand solvation on metal ion complex stability constants should be very important in biological systems where donor groups are frequently forced to be close to one another or in some way are shielded from solvation. In this respect the terminology suggested by Busch[58] of *multiple juxtapositional fixedness* is an appropriate description. As with the macrocyclic effect the cause of enhanced metal binding is a combination of more favorable enthalpy terms from diminished solvation of donor groups and smaller loss of ligand configurational entropy. It is important to keep in mind that the magnitude of metal binding constants to larger molecules could be increased by many orders of magnitude due to these factors as well as the possibility that steric hindrance might have just the opposite effect.

The hydrophobic effect[59] is another aspect of ligand solvation which could be important in determining the stability constants of complexes. However, this effect should not increase the stability of a macrocyclic ligand over an open-chain ligand. In the case of the polyamines, differences in the extent of hydrogen bonding of water to the nitrogen atoms appear to be the dominant ligand-solvation effect.

Finally, if ligand solvation is important in the thermodynamics of metal complexation, then it should also be important in the kinetics of metal complexation, but once again very little attention has been directed to this effect.

Acknowledgment. This work was supported by National Science Foundation Grant GP 14781X.

Registry No. [14]ane$N_4Ni^{II}(ClO_4)_2$, 38643-78-6; C(5,12)-*ms*-Me_2[14]ane$N_4Ni^{II}(ClO_4)_2$, 52610-58-9; C(5,12)-*rac*-Me_6[14]aneN_4-$Ni^{II}(ClO_4)_2$, 52553-45-4; C(5,12)-*ms*-Me_6[14]ane$N_4Ni^{II}(ClO_4)_2$, 25504-25-0; 2,3,2-tet$Ni^{II}(ClO_4)_2$, 27537-50-4.

---

(58) D. H. Busch, K. Farmery, V. Goedken, V. Katovic, A. C. Melnyk, C. R. Sperati, and N. Tokel, *Advan. Chem. Ser.*, No. **100**, 52 (1971).

(59) C. Tanford, "The Hydrophobic Effect: Formation of Micelles and Biological Membranes," Wiley-Interscience, New York, N. Y., 1973, p 21.

Contribution from the Department of Chemistry,
University of Canterbury, Christchurch, New Zealand

Kinetics and Steric Course of the Acid Hydrolysis of *trans*-(Ammine)(diethylenetriamine)(dichloro)cobalt(III) Cation

M. CLAIRE COULDWELL and D. A. HOUSE*

Received May 2, 1974 AIC40286V

Solutions of the title cation, when treated with excess OH^- and then acidified, form the *trans*-diaqua ion. This slowly ($t_{1/2}$ = *ca.* 30 min at 25.0°) isomerizes to an isomeric diaqua ion which we believe is the *a*-ammine-*bc*-diaqua-*dfe*-(diethylenetriamine)cobalt(III) cation, with the diethylenetriamine in the facial configuration (henceforth designated cis). The final products in the uncatalyzed acid hydrolysis of the *trans*-dichloro ion are an equilibrium *cis*-diaqua–*cis*-aquachloro mixture. The rate of acid hydrolysis of the *trans*-dichloro ion has been measured both spectrophotometrically and by chloride release. In 0.3 *F* HNO_3 at 25.0°, the first-order rate constants for the primary hydrolysis are 10^5k_{spectro} (sec^{-1}) = 39.8 ± 0.3 and 10^5k_{Cl} (sec^{-1}) = 52.1 ± 0.8. These data have been interpreted in terms of a mechanism whereby the *trans*-dichloro cation hydrolyzes in acid solution to produce three five-coordinate intermediates. Aquachloro products from two of these have been detected spectrophotometrically in solution (as an 80:20 isomeric mixture) and the slower reacting major component has the above cis configuration. The other aquachloro ion isomerizes rapidly ($t_{1/2}$ = *ca.* 9 min at 25.0°) to the *cis*-aquachloro form and is assigned a *trans*-aquachloro configuration with the secondary NH proton of the meridional diethylenetriamine ligand adjacent to the aqua ligand. It is estimated that 50 ± 10% of the *cis*-aquachloro is formed directly from the *trans*-dichloro complex. The rate of acid hydrolysis of the *cis*-aquachloro isomer has been measured by chloride release and in 1.0 *F* HNO_3 at 25.0°: 10^5k_{Cl} (sec^{-1}) = 7.89 ± 0.28, E_a (kJ mol^{-1}) = 96.3 ± 2.1, ΔS°_{298} ($\text{J K}^{-1}\ \text{mol}^{-1}$) = −8.4 ± 4.2, log *PZ* (sec^{-1}) = 12.75. The *cis*-aquachloro–*cis*-diaqua equilibrium lies substantially (90%) toward the diaqua product.

Introduction

Recent studies[1] of the rate and steric course of the acid hydrolysis of tetraaminedichlorocobalt(III) complexes have been concentrated on systems containing linear[2-5] or macrocyclic[6-8] polyamines. In particular, in the primary hydrolysis of *trans*-$CoCl_2(N_4)^+$ complexes,[9] with N_4 = trien = 2,2,2-tet,[3] 2,3,2-tet,[4] and 3,2,3-tet,[5] there is 0%, *ca.* 50% (meso isomer), and 100% retention of configuration, respectively. However, with N_4 = cyclam = 2,3,2,3-tet[6] and Me_6-2,3,2,3-tet,[7,8] the trans configuration is retained in the aquachloro product.

To provide further insight into these processes, we have investigated the rate of acid hydrolysis and the steric course in the aquation of *trans-af,b,cde*-$CoCl_2(NH_3)(dien)^+$.[10]

Experimental Section

Commercially available diethylenetriamine was used without

---

(1) C. K. Poon, *Inorg. Chim. Acta, Rev.*, 123 (1970).

(2) A. M. Sargeson and G. H. Searle, *Nature (London)*, 200, 356 (1963).

(3) A. M. Sargeson and G. H. Searle, *Inorg. Chem.*, 6, 2172 (1967).

(4) R. Niththyananthan and M. L. Tobe, *Inorg. Chem.*, 8, 1589 (1969).

(5) M. D. Alexander and H. G. Hamilton, *Inorg. Chem.*, 8, 2131 (1969).

(6) C. K. Poon and M. L. Tobe, *J. Chem. Soc. A*, 2069 (1967).

(7) J. A. Kernohan and J. F. Endicott, *Inorg. Chem.*, 9, 1504 (1970).

(8) W. K. Chau and C. K. Poon, *J. Chem. Soc. A*, 3087 (1971).

(9) Abbreviations used: en = $NH_2(CH_2)_2NH_2$, tmd = $NH_2(CH_2)_3$-NH_2, dien = $NH_2(CH_2)_2NH(CH_2)_2NH_2$, trien = $NH_2(CH_2)_2NH(CH_2)_2$-$NH(CH_2)_2NH_2$, 2,3,2-tet = $NH_2(CH_2)_2NH(CH_2)_3NH(CH_2)_2NH_2$, 3,2,-3-tet = $NH_2(CH_2)_3NH(CH_2)_2NH(CH_2)_3NH_2$, cyclam = 1,4,8,11-tetraazacyclotetradecane = 2,3,2,3-tet, Me_6-2,3,2,3-tet = 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane, ox = $C_2O_4^{\,2-}$.