Metal-Ion Recognition by Macrocyclic Ligands. Thermodynamic Stabilities of Nickel Complexes of a Series of O₂N₂-Donor Macrocyclic Ligands

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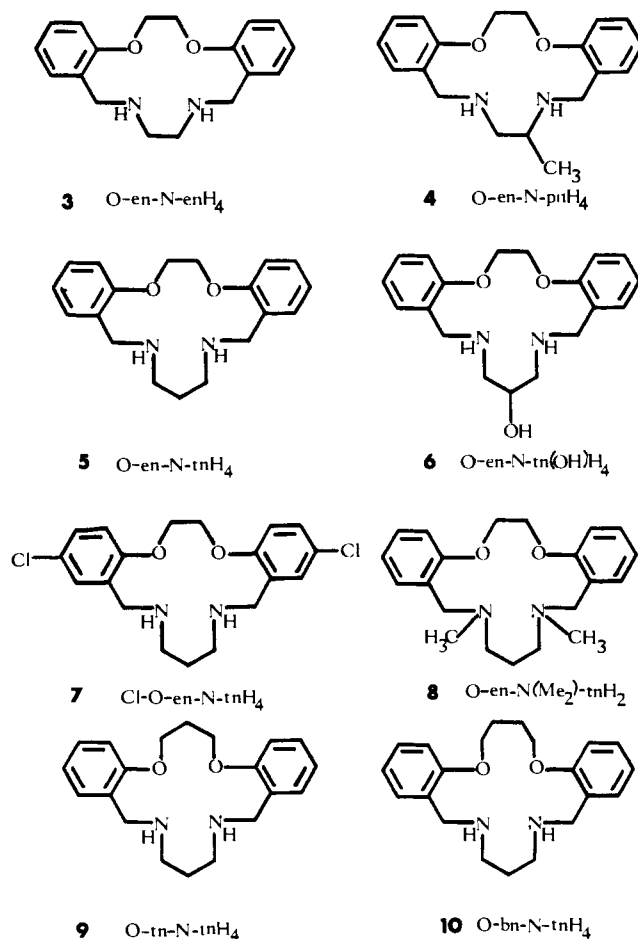Queensland 4811, Australia. Received September 17, 1979*

Abstract: The thermodynamic stabilities of a series of six-coordinate nickel complexes of related 14- to 17-membered macrocyclic ligands incorporating O₂N₂-donor sets have been determined potentiometrically in 95% methanol ($I = 0.1$) and in water ($I = 0.1$ or 1). Both the nature of ligand substituents as well as the size of the macrocyclic ring influence the relative stabilities of the complexes. For the complexes of the unsubstituted 14- to 17-membered ligand series, the stabilities reach a peak at the 16-membered ring complex and consideration of structural factors suggests that this complex incorporates the macrocyclic ring of best fit for nickel(II). Complementary kinetic data for the dissociation of the complexes in acid indicate that the dissociation rates closely parallel the respective log K values; the contribution of macrocycle complexation to the observed peak in thermodynamic stabilities appears to be minor.

Introduction

The alkali and alkaline earth metal-ion selectivity of polyether macrocyclic ligands of the cyclic and bicyclic classes has been well investigated.[2-4] Along a given series of ligands, maximum stability is usually observed when optimum macrocyclic ring (or cavity) size is reached for a particular metal ion. In contrast, such macrocyclic ring size discrimination involving transition-metal ions has been much less documented.[5-8] A major difficulty with these systems when the macrocyclic ligand contains an N₄-donor set is that traditional methods of determining stability constants (such as potentiometric titration) are not always satisfactory with such complexes because thermodynamic equilibrium is often extremely slow to be established.[8-10] Nevertheless, studies involving potentiometric determination of stability constants for nickel complexes of a number of mixed donor macrocycles such as **1** or **2** indicate that equilibrium is established moderately rapidly (<30 min) for such systems.[11]

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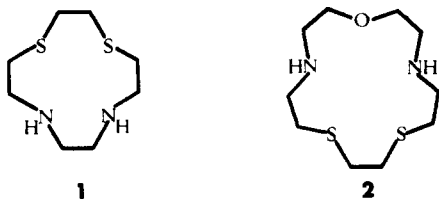
Previously we have reported synthetic[12] and kinetic (formation[13] and dissociation[14]) aspects of nickel complexes of O₂N₂ macrocycles of which **3–10** are typical.[15] The macrocycles have been shown to react with nickel halides to yield only 1:1 complexes of type Ni(macrocycle)X₂ (X = Cl, Br, NCS).[12] These high-spin complexes have been assigned pseudooctahedral geometries both in the solid and in solution and such (trans) pseudooctahedral geometries have been confirmed for the complexes of **5**[13] (containing axial chloro ligands) and **9**[16] (containing axial bromo ligands) by X-ray diffraction. For these complexes, ligand field strength showed the expected[17] diminution with increase in macrocyclic ring size. Studies involving the effects of macrocyclic ring size on the kinetic and thermodynamic stabilities of these nickel complexes are thus not complicated by the coordination number and spin-state changes along the series found for nickel complexes of N₄-donor macrocycles (for example, of the cyclam class).[5]

3 O–en–N–enH₄   **4** O–en–N–pnH₄

5 O–en–N–tnH₄   **6** O–en–N–tn(OH)H₄

7 Cl–O–en–N–tnH₄   **8** O–en–N(Me₂)–tnH₂

9 O–tn–N–tnH₄   **10** O–bn–N–tnH₄

A study of the dissociation in aqueous acid of a series of nickel complexes of these O₂N₂-donor macrocycles has revealed that the observed first-order dissociation rate constants are independent of acid concentration.[14] For the complexes of the 14- to 17-membered unsubstituted macrocycles, a clear-cut relationship between macrocycle ring size and kinetic lability has been established: the dissociation rate reaches a minimum at the 16-membered ring complex.

A comparative investigation of the thermodynamic stabilities of the nickel complexes of **3–10** in water and 95%

methanol is now presented together with the results of a kinetic study of their dissociation in methanolic acid.

Experimental Section

Reagents. All reagents were AR grade unless otherwise specified. Potassium chloride (aqueous studies) and tetramethylammonium chloride (methanol studies) were chosen as supporting electrolytes because the complexes were generally more soluble in chloride media than in solutions containing anions such as nitrate or perchlorate. In addition, chloride ion (unlike other ions such as acetate) has been shown[18] to have no effect on the dissociation kinetics of these nickel complexes.

Tetramethylammonium chloride (Fluka, puriss) was recrystallized from methanol/acetone and then dried under a vacuum for 48 h at room temperature before use.

Tetramethylammonium hydroxide pentahydrate was prepared by a modification of a previous synthesis.[19] To tetramethylammonium chloride (40 g) in dry methanol (80 mL) was added potassium hydroxide (20 g) in methanol (80 mL). The mixture was stirred at room temperature for 2 h and the resulting precipitate of potassium chloride was then filtered off. Water (45 mL) was added to the filtrate (160 mL) and the mixture was concentrated (at 35 °C) to 45 mL under vacuum. The flask was then stoppered and the solution was cooled to 0 °C for 48 h. The colorless needles (15 g) of product were filtered off and washed with cold water and then acetone. The product was stored under a vacuum over soda lime. All operations in the above procedure were carried out under an atmosphere of dry nitrogen.

Magnesium-dried, fractionated AR methanol and doubly distilled water were used in the preparation of all solutions. All solvents were degassed before use by bubbling dry nitrogen through them and were protected from carbon dioxide by a trap containing self-indicating soda lime.

Tetramethylammonium hydroxide (0.1 M) in 95% methanol was prepared by dissolving tetramethylammonium hydroxide pentahydrate (18.12 g) in water (41 mL) and then diluting the solution with absolute methanol until the total volume was 1 L. This solution was standardized by titration with AR Volucon hydrochloric acid using methyl red as indicator.

The analytically pure ligands and metal complexes were prepared as described elsewhere.[12] The nickel stock solution was analyzed gravimetrically using dimethylglyoxime.

Log K Determinations. The potentiometric apparatus consisted of a water-jacketed measuring cell containing a Philips glass electrode (GA-110) and a water-jacketed calomel reference electrode connected by a salt bridge. A common supporting electrolyte (KCl or tetramethylammonium chloride) was used in the reference cell, the measuring cell, and the salt bridge. The temperature was maintained at 25 ± 0.1 °C. During each run water-saturated or dry methanol-saturated nitrogen was bubbled slowly through the solution in the measuring cell. A solution of base (potassium hydroxide or tetramethylammonium hydroxide) was introduced into the measuring cell using a Metrohm Dosimat automatic titrator; the solution in the measuring cell was stirred magnetically. The titration data were obtained in the form of millivolts (to ± 0.1 mV) vs. milliliters of base added; an Orion Model 801A or a Corning 130 pH meter was employed. The apparatus was calibrated daily by titration of a calibration solution with standard base.

In a typical determination of ligand protonation constants, analyzed ligand (2.00×10^{-3} M) in 50 mL of 4.00×10^{-3} M HCl solution ($I = 0.1$ or 1) was titrated with base. Titration steps of between 0.02 and 0.1 mL were chosen such that the voltage change between successive points did not exceed 6.0 mV. Sufficient time was allowed between successive additions to permit equilibrium to be reached (typically 10–30 min). Protonation constants were calculated using the program KONST.[20]

The stability constants for the nickel complexes were determined by a procedure similar to the above, except that the titration was carried out in the presence of nickel ion. The solution to be titrated was prepared by either dissolving the required analyzed solid complex of type Ni(macrocycle)Cl$_2$ or by adding an aliquot of a stock metal chloride solution to a solution of the analyzed ligand. As for the ligand protonation constants, the stability constants were calculated using the program KONST.[20]

Macrocycle concentrations of $\sim 2 \times 10^{-3}$ M for the studies in 95% methanol and $\sim 1 \times 10^{-3}$ to $\sim 2 \times 10^{-3}$ M for the aqueous studies were employed. The majority of the determinations were performed using
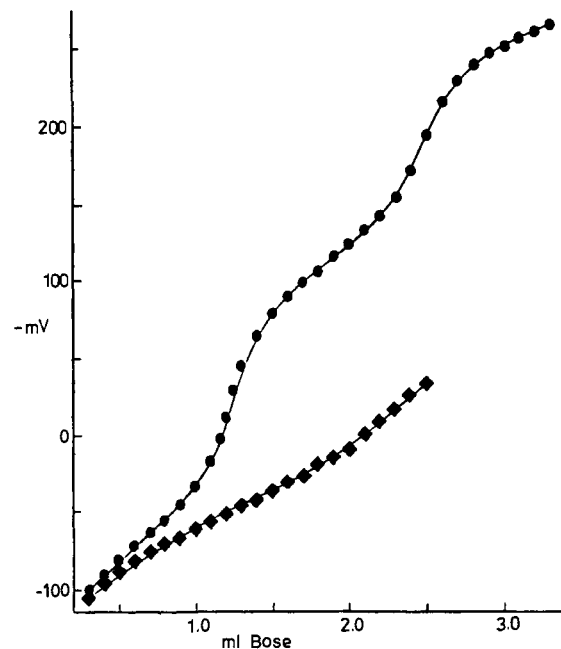
Figure 1. Titration curves: (●) 50 mL of protonated ligand **7**, H_2L^{2+} (2.00×10^{-3} M) with $(CH_3)_4NOH$ (8.27×10^{-2} M); (◆) 51 mL of protonated ligand **7**, H_2L^{2+} (1.96×10^{-3} M) plus Ni^{2+} (3.61×10^{-3} M) with $(CH_3)_4NOH$ (8.27×10^{-2} M).

solutions containing a metal to ligand ratio of either 1:1 or 2:1, and for several systems studies were performed on solutions containing two different metal to ligand ratios. The individual values quoted are the mean from at least two (and up to seven) separate titrations.

Determination of the protonation constants for O-tn-N-tnH$_4$ in the presence of a fourfold excess of KCl in 95% methanol [$I = 1$, $(CH_3)_4NCl$] led to no change in the previous values (found: log K_1 = 10.12; log K_2 = 7.10). Thus competitive complexation by K$^+$ is not likely to be a significant source of error for the determinations in water for which KCl was the inert salt.

Dissociation Kinetics. In a typical experiment a 95% methanol solution of the complex was mixed with an equal volume of 0.2 M HCl in 95% methanol. Complex concentrations were between 10^{-2} and 10^{-3} M; 95% methanol was obtained by diluting 5 mL of water to 100 mL with magnesium-dried methanol. The dissociation of the complexes was followed spectrophotometrically (using a stopped-flow apparatus where necessary) at the wavelengths of the $^3A_{2g} \rightarrow {}^3T_{1g}$ transition (600–650 nm). Details of the apparatus and treatment of data are given elsewhere together with details of the dissociation rate studies in aqueous media.[18] All quoted first-order rate constants are the average of between two and eight individual determinations. The rate constants were independent of the concentration of the complex and also were acid independent over the range studied (0.05–1.0 M). Hence the acid merely acts as a scavenger for the free ligand once it dissociates from the nickel. A similar situation was found to occur for the dissociation studies in aqueous media.[18]

Results and Discussion

Protonation Constants for the Macrocycles. The protonation constants K_1 and K_2 were determined potentiometrically by titration of the respective ligand hydrochlorides with base where

$$K_1 = [HL^+]/[L][H^+] \qquad K_2 = [H_2L^{2+}]/[HL^+][H^+]$$

Owing to the very low solubility of the unprotonated free ligands in water, it was only possible to obtain constants in this solvent (at $I = 0.1$ and/or 1.0, KCl) for four of the ligands. To overcome this difficulty, the bulk of the studies were performed using 95% methanol [$I = 0.1$, $(CH_3)_4NCl$] as solvent. The titration curves generally showed two inflection points corresponding to the neutralization of the two amine functions of each ligand (a typical curve is illustrated in Figure 1). However, because of precipitation of the neutralized ligand, it was

Table I. Thermodynamic and Kinetic (Complex Dissociation) Data for the Macrocyclic Systems ($t = 25\ °C$)

ligand (ring size)	medium[a]	ligand[b,c] log K_1	log K_2	complex (NiL^{2+}) log K^{c-e}	dissociation rate[e-g] k_d, s^{-1}
3, O-en-N-enH₄ (14)	M ($I = 0.1$)	9.19	5.40	3.7 ± 0.2	6.9 ± 0.4
4, O-en-N-pnH₄ (14)	M ($I = 0.1$)	9.48	4.98	3.5 ± 0.3	(5.2 ± 0.3) × 10⁻¹
	W ($I = 1.0$)	9.41	6.01		(1.4 ± 0.1) × 10⁻¹
5, O-en-N-tnH₄ (15)	M ($I = 0.1$)	9.81[h]	6.82	5.4 ± 0.1[i]	(1.1 ± 0.1) × 10⁻²
	W ($I = 0.1$)	9.69	7.63	5.1 ± 0.2	
	W ($I = 1.0$)	9.96	8.01	5.4 ± 0.2	(3.5 ± 0.3) × 10⁻³
6, O-en-N-tn(OH)H₄ (15)	M ($I = 0.1$)	9.45	6.49	5.4 ± 0.1	(2.3 ± 0.2) × 10⁻¹
7, Cl-O-en-N-tnH₄ (15)	M ($I = 0.1$)	9.36	6.29	4.8 ± 0.1	
8, O-en-N(Me₂)-tnH₂ (15)	M ($I = 0.1$)	9.64	6.61	<4	
	W ($I = 1.0$)	10.14	7.92	<4	(3.8 ± 0.3) × 10⁻⁴
9, O-tn-N-tnH₄ (16)	M ($I = 0.1$)	10.07	7.09	5.8 ± 0.1	(5.4 ± 0.3) × 10⁻³
	W ($I = 0.1$)	9.95	7.71	5.2 ± 0.2	
	W ($I = 1.0$)	10.14	8.07	5.5 ± 0.2	(6.4 ± 0.4) × 10⁻⁴
10, O-bn-N-tnH₄ (17)	M ($I = 0.1$)	9.63	8.10	3.5 ± 0.3	>0.5

[a] M = 95% methanol; W = water. [b] Log K_1 = [LH]/[L][H]; log K_2 = [LH₂]/[LH][H]. [c] Inert salt: KCl for aqueous studies, $(CH_3)_4NCl$ for 95% methanol studies. [d] For the equilibrium $Ni^{2+} + L \rightleftharpoons NiL^{2+}$. [e] Errors represent an estimate of total uncertainty. [f] Values for aqueous 1 M HCl and 0.1 M HCl in 95% methanol. The corresponding k_d values (s^{-1}) for 0.05 M HCl and 95% methanol [$I = 0.1$, $(CH_3)_4NCl$]: ligand **3**, 6.6 ± 0.4; ligand **4**, (4.8 ± 0.3) × 10⁻¹; ligand **5**, (1.2 ± 0.1) × 10⁻²; ligand **6**, (2.2 ± 0.2) × 10⁻¹; ligand **9**, (5.7 ± 0.3) × 10⁻³. [g] Details of the aqueous k_d determinations are given in ref 17. [h] The corresponding log K values in 90% methanol are 9.42 and 6.50. [i] The corresponding log K value in 90% methanol is 5.2 ± 0.1.
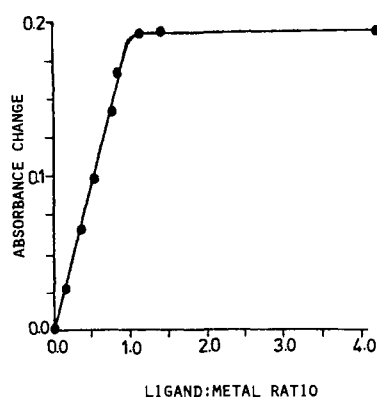

Figure 2. Plot of absorbance change at 655 nm (corrected for absorbance of uncomplexed $NiCl_2$) vs. ligand:metal ratio for nickel chloride plus ligand **9** in methanol ($[Ni^{2+}]_{total} = 9.2 \times 10^{-3}$ M).

not possible to obtain a complete set of data for certain systems.

Log K_1 values of between 9.2 and 10.1 and log K_2 values between 5.0 and 8.1 were obtained (Table I); thus the ligands are moderately strong bases.[21] The values appear generally similar to those reported for other macrocyclic systems containing two secondary amine nitrogen donors.[4,11]

Stability Constants for the Nickel Complexes. Potentiometric measurements have been used to determine stability constants (K) for the 1:1 (metal to ligand) nickel complexes of ligands **3–10**. Because of precipitation (complex, ligand, or nickel hydroxide), it was not possible to obtain the complete titration curve for any of the systems studied and for some systems only an approximate log K value could be obtained. A typical titration curve is shown in Figure 1. The titration data were fitted assuming the presence of 1:1 metal:ligand species:

$$Ni^{2+} + L \overset{K}{\rightleftharpoons} NiL^{2+}$$
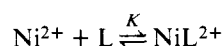
In all cases satisfactory fits of the data were obtained and no improvement occurred when species of type ML_2^{2+} were included. It is perhaps significant that only 1:1 products were obtained in the solid state. Moreover, where solubility permitted, spectrophotometric titrations in methanol gave simple 1:1 end points;[22] there was no evidence for the formation of species other than ML^{2+} even when the ligand was present in considerable excess (see Figure 2).

Log K values for the complexes are listed in Table I. Comparison of the values in 95% methanol [$I = 0.1$ M, $(CH_3)_4NCl$][23] with the limited data obtained in water ($I = 0.1$ M, KCl) shows that the latter values are slightly lower than those obtained in methanol—a similar trend to that noted for other systems.[4] Since there is competition between the solvent and the macrocycle for the metal ion, the slightly lower log K values in water very likely reflect the greater solvating ability of water toward nickel.

Effects of Macrocycle Structure on Log K Values. The incorporation of a hydroxyl substituent on the aliphatic backbone of the 15-membered macrocycle (to yield **6**) has no significant effect on the stability of its nickel complex, while chloro substituents on the aromatic rings (ligand **7**) result in a small decrease in stability compared with **5**. N-Methylation, as has occurred in ligand **8**, results in the usual[24,25] reduction in the stability of the nickel complex, presumably as a result of steric hindrance.

The log K values (Table I) for the nickel complexes indicate that stabilities follow the ligand order **3** < **5** < **9** > **10**. That is, the stabilities follow the macrocyclic ring size sequence 14 < 15 < 16 > 17 (Figure 3). The peak in stability at the 16-membered ring complex provides a clear example of macrocyclic ring size control of thermodynamic stability for a series of related nickel complexes.

Hole-size considerations based on crystallographic data also suggest that the 16-membered macrocycle provides the fit of lowest strain for nickel(II), although the optimum hole size may lie somewhere between those of the 15- and 16-membered rings. A search of the literature for X-ray data for complexes of high-spin nickel(II) bound to ligands containing ether oxygen donor atoms indicated a mean (eight distances) nickel–oxygen bond length of 2.15 Å for such complexes.[26] Since a bond distance of about 2.10 Å is typical of sp³-hybridized nitrogens bound to nickel(II),[13] an optimum macrocyclic hole size of approximately 4.25 Å seems reasonable for the present series. This is slightly larger than that of 4.20 Å found for the sum of the mean nickel–oxygen and nickel–nitrogen distances in the nickel complex of the 15-membered macrocycle **5**,[13] but closer to that of 4.28 Å found for the nickel complex of the 16-membered analogue **9**.[16]

Further Thermodynamic Considerations. Since the effects of macrocyclic ring size on complex stability might be expected to be better understood if corresponding ΔH and ΔS data were available, the stabilities of the nickel complexes of the 15- and

Table II. Effect of Temperature on the Macrocycle Protonation Constants of **3** and **7** and on the Corresponding Nickel Complex Stability Constants[a]

temp,[b] °C	ligand[c] log $K_1{}^d$	log $K_2{}^d$	complex (NiL^{2+}) log K^d
	5, O-en-N-tnH₄		
20.4	9.91	6.91	5.4
25.0	9.81	6.83	5.4
32.8	9.62	6.61	5.5
39.0	9.52	6.43	5.5
	9, O-tn-N-tnH₄		
19.5	10.19	7.25	5.9
25.0	10.07	7.08	5.8
39.1	9.60	6.87	5.9

[a] For I = 0.1 M, $(CH_3)_4NCl$ in 95% methanol. [b] Temperatures accurate to ±0.1 °C. [c] Values quoted are an average of two or three individual determinations. [d] The ligand log K values are estimated to have an uncertainty of ±0.05, whereas the log (stability constant) values are estimated to be ±0.1.

16-membered macrocycles **5** and **9** were determined at a series of temperatures between 20 and 40 °C in order to calculate such data. However, although for these ligands both protonation constants showed a progressive decrease with increase in temperature (Table II), the respective log K values for nickel complex formation were independent of temperature (within experimental error) over the range studied (Table II). ΔH and ΔS values have been estimated using $\Delta H/RT - \Delta S/R = -\ln K$; however, because of likely errors which are inherent in the experimental procedure used for the determinations,[8] the values must be considered tentative. For the complexes of **5** and **9**, enthalpies of complexation (ΔH_c) of approximately zero in each case and entropies ($\Delta S_c = -R \ln K$) of very approximately 103 and 113 J K^{-1} mol^{-1} were obtained, respectively. Hence, for these complexes, complex formation appears to be entropy governed.

Previous work[27] involving a calorimetric comparison of the interaction of bis(2-aminoethyl) ether and diethylenetriamine with nickel(II) has demonstrated that there is a less favorable enthalpic contribution for the ether-containing ligand complex; it was postulated that the coordination of the ether oxygen to nickel might be considered to be an endothermic process. This contrasts with the exothermic coordination of the secondary amine of diethylenetriamine to nickel. Thus the approximately zero ΔH values found for the complexes of **5** and **9** could largely reflect the presence of two ether oxygen and two secondary nitrogen donors in each of these complexes.

Dissociation Kinetics. A study of the dissociation kinetics of nickel complexes of the O₂N₂-donor macrocycles in aqueous 1 M acid is now complete.[14,18] However, because of the small number of log K determinations that were possible in aqueous solution, only a very limited comparison of these thermodynamic data with the aqueous dissociation data has been possible (Table I). In view of this, a parallel investigation of the dissociation kinetics of the nickel complexes in 95% methanol has been carried out.

Table I lists the first-order rate constants for the dissociation of the complexes of **3–6, 9,** and **10** in 0.1 (and 0.05) M HCl in 95% methanol. As for the studies in aqueous media, there is no significant difference between the observed rate constants at these two acid concentrations. Similarly, there is a dependence of the dissociation rate on macrocycle ring size and, as before, the nickel complex of the 16-membered ring ligand shows the minimum rate. The kinetic labilities follow the ring-size sequence 14 > 15 > 16 < 17; along this series the half-lives (in s) are 0.1, 63, 128, and <1.4, respectively.[28]

The complementary thermodynamic and kinetic data for the present systems (Table I) thus indicate that the stabilities
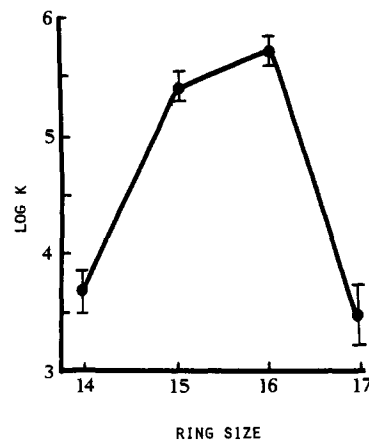
Figure 3. Log K vs. ring size for Ni(II) complexes of the unsubstituted O₂N₂-donor macrocycles **3, 5, 9,** and **10**.

show a similar trend to the corresponding dissociation rates. This correspondence parallels the results from a previous study[6] [involving copper(II) complexes of a series of S₄-donor macrocycles] in which a related dependence of dissociation rates and thermodynamic stabilities was shown to occur. For this latter system, ring size was demonstrated to have a much greater influence on the respective dissociation rates than on the formation rates. The complementary trends in the log K and dissociation rate data suggest that such a situation also occurs for the present systems.[29]

Concluding Remarks

It has been well demonstrated previously[5,17,30,31] that complexes of macrocyclic ligands are generally more kinetically inert and thermodynamically stable than the complexes of corresponding open-chain ligands. The present results provide a clear example of the manner in which small changes in macrocycle hole diameter (of the order of 0.05–0.1 Å between successive members of the 14- to 17-membered macrocycles) for a series of related nickel complexes can markedly influence such kinetic and thermodynamic properties.

Effects which broadly parallel those discussed here very likely also occur in a number of biological metallo systems. It seems that such effects could form the basis for the recognition mechanism for specific metal ions which is a characteristic of many such systems. Indeed, preliminary studies involving the interaction of the above series of ligands with a number of other transition-metal ions indicate a range of very different thermodynamic and kinetic behavior and such variation may provide a basis for the development of efficient metal-ion discrimination procedures for these ions. Further studies in this area are proceeding.

Supplementary Material Available: A listing of data giving details of individual determinations of ligand protonation constants and nickel complex log K values (2 pages). Ordering information is given on any current masthead page.

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(21) Macrocyclic ring size is found to have only a small effect on the respective log K_1 values, whereas log K_2 values increase steadily as ring size increases. This is in accord with the postulate that, for the smaller rings, electrostatic repulsions between the two quaternary protons will be enhanced owing to smaller interproton distances. This observation parallels that made elsewhere for 4N-donor macrocycles (where the third and fourth log K values showed a similar trend to that just discussed). See: Leugger, A. P.; Hertli, L.; Kaden, T. A. *Helv. Chim. Acta* **1978**, *61*, 2296–2306.
(22) To avoid possible complications arising from competitive ligand protonation by water, the titrations were performed in absolute methanol (Karl Fischer determination gave a water content of <0.01% by weight) using anhydrous nickel chloride (see ref 13). A more comprehensive set of titrations in

anhydrous dimethyl sulfoxide also gave only 1:1 end points.
(23) To check whether variation in the water content of the aqueous methanol was likely to cause significant errors in the respective constants, the value for the Ni(II) complex of **5** was determined in both 90 and 95% methanol. Log K values of 5.2 ± 0.1 and 5.4 ± 0.1 were obtained, respectively. Thus any small experimental inaccuracies in the water content for the determinations involving 95% methanol will not have any significant effect on the log K values obtained.
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(28) The corresponding values found in the studies using aqueous media are 0.8, 198, 1083, and <1.4 s (see ref 18).
(29) Although with simple ligands the complexation of nickel(II) is commonly found to be second order and is usually postulated to follow a dissociative ion-pair (I_d) mechanism, with macrocyclic ligands the mechanism is often more complicated than this. Indeed, although we were unable to follow the formation kinetics in water because of low solubilities, it has been previously demonstrated (ref 13) that the complexation of **5** and **9** with nickel in methanol consists of two sequential steps—the first of which is second order and is controlled by the rate of methanol exchange for nickel while the second (first order) step was postulated to involve rearrangement of the ligand within the coordination sphere. Thus, for the above studies in absolute methanol, the relationship $K = k_f/k_d$ is not applicable (see: Margerum, D. W.; Cayley, G. R.; Weatherburn, D. C.; Pagenkopf, G. K. "Coordination Chemistry", *ACS Monogr.* **1978**, No. 174, 85) and, by analogy, this also seems likely to be so for the present studies in water and 95% methanol. Nevertheless, the values for the product $k_d K$ vary by approximately an order of magnitude, whereas the variation in the dissociation rate is about 10³; this is consistent with the variation in the respective log K values being largely controlled by complex dissociation.
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Theory of Hyperfine Interaction in Five-Liganded Divalent and Trivalent Manganese Porphyrin Systems

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Abstract: As part of a program for studying the electronic structures and associated properties of heme and hemoglobin systems with the iron atom replaced by other atoms, such as manganese and cobalt, we have studied in the present work two high-spin manganese porphyrin systems, divalent H_2O-manganese porphyrin ($S = 5/2$) and trivalent Cl-manganese porphyrin ($S = 2$). The charge and spin distributions over these molecules have significant overall similarities with the corresponding heme systems involving iron as central atom, indicating in particular that the metal atom is close to neutrality and a substantial part of the unpaired spin population, about 30%, is drained away toward the neighboring atoms, the major part of this unpaired spin population appearing on the nitrogen atoms of ligand pyrrole rings and the fifth ligand. The hyperfine interaction tensors for the ^{55}Mn and ^{14}N nuclei have been analyzed using the calculated electronic wave functions and spin distributions for the two molecules. The results for ^{55}Mn in the divalent system, which is the only case for which experimental data are available, are in good agreement with experiment for the isotropic component of the hyperfine tensor and the component parallel to the plane of the porphyrin, the experimental value for the perpendicular component being somewhat (about 25%) higher than theory. Suggestions are made for bridging this difference between theory and experiment. It is hoped that experimental data on the ^{14}N hyperfine interaction in the divalent system and ^{55}Mn and ^{14}N hyperfine interactions in the trivalent compound will be available in the near future to allow comparison between theory and experiment, and further test the small but significant differences in charge and spin distributions found in these porphyrin systems when iron is replaced by manganese.

I. Introduction

The study of the electronic structures of manganese porphyrin compounds by themselves or attached to proteins is important both because of the relationship of these compounds to the corresponding iron compounds as well as for the understanding of the origin of their properties, among them