First Potentiometric Determination of Stability Constants of Nickel(II) Complexes with Tetra-azacycloalkanes

Mauro Micheloni, Piero Paoletti,* and Antonio Sabatini
Istituto di Chimica Generale ed Inorganica, Università di Firenze and I.S.S.E.C.C. C.N.R., Via J. Nardi 39, 50132 Florence, Italy

The stability constants of nickel(II) complexes with 1,4,7,10-tetra-azacyclotetradecane (L^1), 1,4,8,12-tetra-azacyclopentadecane (L^2), and 1,5,9,13-tetra-azacyclohexadecane (L^3) have been determined by a ' batchwise ' potentiometric technique at 25 °C in 0.5 mol dm^{-3} KNO_3. Ligand L^2 forms the strongest complex (log K = 18.38), L^1 the next strongest (log K = 14.81), and L^3 the weakest of the three (log K = 13.23). By combining the standard free energies for complex formation with the standard enthalpies obtained previously, the entropy contributions have been calculated and are discussed. The three ligands all form monoprotonated complexes $[Ni(HL)]^{3+}$ and their stability constants have been determined. The stabilities of the 1 : 1 complexes $[NiL]^{2+}$ have been compared with those of the corresponding complexes with the analogous open-chain ligands. The macrocyclic complexes are more stable than the corresponding complexes with non-cyclic tetra-amines. This extra stability (' macrocyclic effect ') is due to a favourable entropy contribution, the enthalpy contribution being unfavourable.

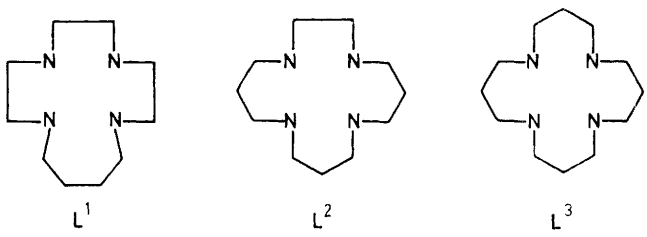
The enthalpy and entropy contributions to the enhanced stability of the copper(II) complexes with saturated tetra-azamacrocycles as compared with the equivalent complexes with non-cyclic polyamines (' macrocyclic effect ') have been widely investigated.[1-5] The determination of the stability constants of the analogous nickel(II) macrocyclic complexes is difficult on account of their kinetic inertness. The only determination of stability constants of saturated nickel(II) complexes available to date is that of complexes with 1,4,8,11-tetra-azacyclotetradecane (cyclam) and two of its *C*-methylated derivatives.[2] These data were obtained by the spectrophotometric method and provide the first estimate of the macrocyclic effect for nickel(II) complexes. On the other hand potentiometric titration is the most widely used for the determination of accurate stability constants in aqueous solution. Unfortunately its application to nickel(II) complexes of macrocyclic ligands is not easy on account of the long times required for chemical equilibrium to be reached.

We have now successfully developed a batchwise potentiometric technique and used it to determine the stability constants of nickel(II) complexes with the ligands 1,4,7,10-tetra-azacyclotetradecane (L^1), 1,4,8,12-tetra-azacyclopentadecane (L^2), and 1,5,9,13-tetra-azacyclohexadecane (L^3).

Experimental

Ligands and Complexes.—The ligands 1,4,7,10-tetra-azacyclotetradecane (L^1) and 1,5,9,13-tetra-azacyclohexadecane (L^3) were prepared by published methods.[6,7] 1,4,8,12-Tetra-azacyclopentadecane (L^2) was obtained from Strem Chemicals and was used without further purification. The complexes were obtained by mixing equimolar amounts of $Ni(ClO_4)_2 \cdot 6H_2O$ and the ligand in hot butanol. The products were recrystallized from ethanol. Elemental analyses were as follows: Found: C, 26.1; H, 5.5; N, 12.1. Calc. for $[NiL^1(ClO_4)_2]$: C, 26.2; H, 5.3; N, 12.25%. Found: C, 28.4; H, 5.7; N, 12.3. Calc. for $[NiL^2(ClO_4)_2]$: C, 28.0; H, 5.55; N, 11.9%. Found: C, 30.0; H, 5.8; N, 11.7. Calc. for $[NiL^3(ClO_4)_2]$: C, 29.65; H, 5.75; N, 11.5%.

Other Reagents.—A stock 0.5 mol dm^{-3} solution of potassium nitrate was prepared from Merck Suprapur grade reagent without further purification and the solution was used as the ionic medium for all potentiometric measurements.



Aqueous solutions containing each complex in the ionic medium, with different amounts of hydrochloric acid were prepared in separate bottles (see Table 1). The magnitude of $-\log[H^+]$ for each solution was measured periodically until a constant value was reached. The pH was measured with a digital potentiometer (Orion model 701A) using a glass electrode (Orion model 91-01), a salt bridge containing the ionic medium, and an Ag–AgCl reference electrode. The temperature of the cell was maintained at 25 ± 0.01 °C. The standard potential of the glass electrode was determined by Gran's method.[8] The systems investigated took a few days to reach equilibrium. The potentiometric data were processed using the computer program MINIQUAD;[9] the resulting stability constants are given in Table 2.

Results and Discussion

1 : 1 *Complexes.*—In aqueous solution the most common stereochemical arrangements of nickel(II) complexes with tetra-azamacrocyclic ligands are octahedral *trans*-diaqua and square planar. In some cases, the two forms co-exist in equilibrium.[10] Under our experimental conditions the complexes formed with L^2 and L^3 appear to have the *trans*-diaqua form; [11,12] the *trans*-diaqua paramagnetic form and the planar diamagnetic form exist in equilibrium when the ligand is L^1.[6] We have calculated the stability constants for each species (see Table 2) by using the known value for the interconversion equilibrium constant.[6] By combining these values with the published $\Delta H^\ominus$ values [6] we have obtained the first thermodynamic parameters $\Delta G^\ominus$ and $\Delta S^\ominus$ for the formation of both paramagnetic and diamagnetic forms. The entropy contribution ($T\Delta S^\ominus$) to the stability of the diamganetic form is very high, even larger than the enthalpy contribution.

The standard free energies for complex formation for the ligands L^2 and L^3 are given in Table 2, and by combining these values with the standard enthalpies obtained previously [12,13] we have calculated the entropy contributions. It will be seen that for both nickel(II) and copper(II) the ligand L^2 forms the strongest complex, L^1 the next strongest, and L^3 the weakest. The $T\Delta S^\ominus$ terms are of similar magnitude, so that variations in $\Delta G^\ominus$ reflect principally the variations in $\Delta H^\ominus$. This can be understood in terms of the geometry of the complexes. The macrocyclic ligand which forms the most stable complex with nickel(II) is cyclam (log K = 21.9),[2] in which the number of atoms in the chelate rings alternates (5,6,5,6). The ligands L^2 and L^3 are related to cyclam by the presence of one and two extra carbon atoms, respectively, giving ring-size sequences of 5,6,6,6 and 6,6,6,6. The ligand L^1 is isomeric with cyclam, but gives a ring-size sequence 5,5,5,7, which is less stable than that of the cyclam complex, less stable than the complex of L^2 which has one carbon atom more, but more stable than the complex of L^3 which has two carbon atoms more. The complexes of nickel(II) show larger variations in stability than do the complexes of copper(II) with the same group of ligands.[4,6,12] This can be attributed to the fact that the copper ion has a greater capacity to adapt to the varying geometrical requirements of the ligands.[14,15]

Table 1. Experimental details of the potentiometric measurements

System	Initial amount (mmol) Ligand	Metal	Acid	$-\log[H^+]$
Ni^{II}–L^1 [a]	0.2624	0.2624	0.0148	7.303
	0.3149	0.3149	0.1156	5.610
	0.2656	0.2656	0.2126	4.762
	0.2648	0.2648	0.3105	4.538
	0.2608	0.2608	0.4088	4.378
	0.2648	0.2648	0.5071	4.225
	0.2642	0.2642	0.6044	4.121
	0.2635	0.2635	0.7026	3.945
	0.2555	0.2555	0.8005	3.363
	0.2668	0.2668	0.8990	2.980
Ni^{II}–L^2 [b]	0.2494	0.2494	0.2671	5.100
	0.2594	0.2594	0.4011	3.827
	0.2275	0.2275	0.5349	3.633
	0.2246	0.2246	0.6688	3.525
	0.2440	0.2440	0.7954	3.175
	0.2509	0.2509	0.9044	3.144
	0.2486	0.2486	1.0135	2.884
	0.2442	0.2442	1.0701	2.717
	0.2313	0.2313	1.1243	2.509
Ni^{II}–L^3 [c]	0.1693	0.1693	0.0635	7.253
	0.1650	0.1650	0.1409	6.930
	0.1651	0.1651	0.2133	6.783
	0.1644	0.1644	0.2551	5.945
	0.1669	0.1669	0.2854	5.908
	0.1642	0.1642	0.3295	5.834
	0.1645	0.1645	0.3568	5.808
	0.1635	0.1635	0.4283	5.696
	0.1585	0.1585	0.4955	5.539
	0.1640	0.1640	0.5514	5.419

Equilibration times: [a] 10 days, [b] 20 days, [c] 8 days.

Monoprotonated Complexes.—The three ligands all form monoprotonated complexes with nickel(II), but the differences in stability are less marked than with the 1 : 1 complexes. The ease of protonation of the 1 : 1 complex decreases as the strength of the latter increases. When one nitrogen is protonated, the macrocyclic ligand is tridentate and has one very large chelate ring containing the $-NH_2^+$ group. It would be useful to know which of the non-equivalent nitrogen atoms is protonated. The values of log K for reaction (i) are given in

$$Ni^{2+} + HL^+ \rightleftharpoons [Ni(HL)]^{3+} \quad \text{(i)}$$

Table 2, and can be compared with values obtained for analogous reactions. For example, the equilibrium constant of reaction (i) when L = L^3 and the stability constant of the nickel(II) complex with 4-azaheptane-1,7-diamine (L^4) are 8.05 and 9.2 respectively; in the L^4 complex there are two adjacent six-membered rings,[16] and the difference in log K is 1.15. The differences (in log K) between the equilibrium constant of reaction (i) when L = L^1 and the stability constants of the nickel(II) complexes with 3-azapentane-1,5-diamine (L^5) and 3-azaheptane-1,7-diamine (L^6) are 2.4 and −0.5, respectively, but it seems most likely that the somewhat strained seven-membered ring is opened by protonation, leaving two five-membered rings adjacent, as in the L^5 complex. The equilibrium constant of reaction (i) when L = L^2 may be compared with the stability constants of the complexes $[NiL^4]^{2+}$ ($\Delta\log K$ = 1.2) or $[NiL^7]^{2+}$ (L^7 = 3-azahexane-1,6-diamine)($\Delta\log K$ = −0.2). The high stability of the complex $[Ni(HL^2)]^{3+}$ and the similarity to the complex $[NiL^7]^{2+}$ suggest that the former complex contains five- and six-membered rings adjacent to each other. We conclude that the site of protonation is determined by the stability of the protonated complex in the case of the ligand L^2, but by the relief of ring strain in the case of the ligand L^1.

Table 2. Thermodynamic parameters, $\Delta G^\ominus$, $\Delta H^\ominus$, and $T\Delta S^\ominus$, of formation of nickel(II) complexes with ligands L^1, L^2, and L^3 in aqueous solution, at 25 °C in 0.5 mol dm^{-3} KNO_3 (standard state = 1 mol dm^{-3})

Ligand	Reaction	log K	$-\Delta G^\ominus$ [a,b] / kJ mol^{-1}	$-\Delta H^\ominus$ / kJ mol^{-1}	$T\Delta S^\ominus$ / kJ mol^{-1}
L^1	$Ni^{2+} + L \rightleftharpoons [NiL]^{2+}_{oct}$	14.81(3)	84.5(2)	53.5(4)	31.0(6)
L^1	$Ni^{2+} + L \rightleftharpoons [NiL]^{2+}_{plan}$	14.83(3)	84.6(2)	36.4(8) [c]	48(2)
L^1	$Ni^{2+} + L + H^+ \rightleftharpoons [Ni(HL)]^{3+}$	19.3(1)	110.1(6)		
L^1	$Ni^{2+} + HL^+ \rightleftharpoons [Ni(HL)]^{3+}$	8.32	47.48		
L^2	$Ni^{2+} + L \rightleftharpoons [NiL]^{2+}_{oct}$	18.38(3)	104.9(2)	75(1) [d]	30(1)
L^2	$Ni^{2+} + L + H^+ \rightleftharpoons [Ni(HL)]^{3+}$	22.04(9)	125.8(5)		
L^2	$Ni^{2+} + HL^+ \rightleftharpoons [Ni(HL)]^{3+}$	10.96	62.55		
L^3	$Ni^{2+} + L \rightleftharpoons [NiL]^{2+}_{oct}$	13.23(2)	75.5(1)	40.6(8) [e]	34.9(8)
L^3	$Ni^{2+} + L + H^+ \rightleftharpoons [Ni(HL)]^{3+}$	18.80(7)	105.7(4)		
L^3	$Ni^{2+} + HL^+ \rightleftharpoons [Ni(HL)]^{3+}$	8.05	45.94		

[a] This work. [b] Values in parentheses are standard deviations in the last significant figure. [c] Ref. 6. [d] Ref. 13. [e] Ref. 12. oct = octahedral; plan = square planar.

Table 3. Macrocyclic effect in Ni^{II} complexes; thermodynamic parameters, $\Delta G^{\ominus}$, $\Delta H^{\ominus}$, and $T\Delta S^{\ominus}$ for the reaction:

$$[NiL_{non\text{-}cyclic}]^{2+}_{oct} + L_{cyclic} \rightleftharpoons [NiL_{cyclic}]^{2+}_{oct} + L_{non\text{-}cyclic}$$

$L_{non\text{-}cyclic}$	L_{cyclic}	$-\Delta G^{\ominus}$ / kJ mol^{-1}	$\Delta H^{\ominus}$ / kJ mol^{-1}	$T\Delta S^{\ominus}$ / kJ mol^{-1}	Ref.
3,6-Diaza-octane-1,8-diamine	L^1	2.43	5.1	7.4	This work, 6, 17
4,7-Diazadecane-1,10-diamine	L^2	21.05	5.3	26.4	This work, 13, 17
4,8-Diazaundecane-1,11-diamine	L^3	15.69	3.5	19.2	This work, 12, 17
3,7-Diazanonane-1,9-diamine	cyclam	33.67	−20.5	13.2	17, 18

Macrocyclic Effect for Ni^{II} *Complexes.*—To evaluate the extent of the macrocyclic effect we have compared the stabilities of the complexes with cyclic ligands and those with open-chain ligands.[17] The contributions of enthalpy and entropy terms to the stabilities of macrocyclic complexes differ substantially from system to system. To evaluate the relative importance of these terms in the nickel systems, we have compared the thermodynamic parameters of a macrocyclic complex with those of the most stable open-chain analogue; the values are given in Table 3. The small macrocyclic effect observed for the complex $[NiL^1]^{2+}$ is due to a favourable entropy term, which overrides the unfavourable enthalpy term. The same applies to $[NiL^2]^{2+}$ and $[NiL^3]^{2+}$, but the entropy terms are larger, so the macrocyclic effect is more marked. By contrast, the macrocyclic effect in [Ni(cyclam)]$^{2+}$ is both due to a favourable enthalpy term and a favourable entropy term (see Table 3).[18]

Acknowledgements

We thank Dr. J. Gelsomini and Mr. V. Nanini for technical assistance.

References

1 D. K. Cabbiness and D. W. Margerum, *J. Am. Chem. Soc.*, 1969, **91**, 6540.
2 F. P. Hinz and D. W. Margerum, *Inorg. Chem.*, 1974, **13**, 2941.
3 M. Kodama and E. Kimura, *J. Chem. Soc., Chem. Commun.*, 1975, 326.
4 A. Anichini, L. Fabbrizzi, P. Paoletti, and R. M. Clay, *J. Chem. Soc., Dalton Trans.*, 1978, 577.
5 R. M. Clay, M. Micheloni, P. Paoletti, and W. V. Steele, *J. Am. Chem. Soc.*, 1979, **101**, 4119.
6 L. Fabbrizzi, M. Micheloni, P. Paoletti, and A. Poggi, *J. Chem. Soc., Dalton Trans.*, 1982, 61.
7 W. L. Smith, J. D. Ekstrand, and K. N. Raymond, *J. Am. Chem. Soc.*, 1978, **100**, 3539.
8 G. Gran, *Analyst*, 1952, **77**, 661; F. J. C. Rossotti and H. Rossotti, *J. Chem. Educ.*, 1965, **42**, 375.
9 A. Sabatini, A. Vacca, and P. Gans, *Talanta*, 1974, **21**, 53.
10 A. Anichini, L. Fabbrizzi, P. Paoletti, and R. M. Clay, *Inorg. Chim. Acta*, 1977, **24**, 21.
11 L. Fabbrizzi, *J. Chem. Soc., Dalton Trans.*, 1979, 1857.
12 E. Gallori, E. Martini, M. Micheloni, and P. Paoletti, *J. Chem. Soc., Dalton Trans.*, 1980, 1722.
13 L. Fabbrizzi, M. Micheloni, and P. Paoletti, *Inorg. Chem.*, 1980, **19**, 535.
14 L. Fabbrizzi, M. Micheloni, and P. Paoletti, *J. Chem. Soc., Dalton Trans.*, 1980, 134.
15 J. Gazo, I. B. Bersuker, J. Garaj, M. Kabesova, J. Kohout, H. Langfelderova, M. Melnik, M. Serator, and F. Valach, *Coord. Chem. Rev.*, 1976, **19**, 253.
16 R. Barbucci, P. Paoletti, and A. Vacca, *Inorg. Chem.*, 1975, **14**, 302, and references therein.
17 R. M. Smith and A. E. Martell, 'Critical Stability Constants,' Plenum Press, New York, 1975, vol. 2.
18 L. Fabbrizzi, P. Paoletti, and R. M. Clay, *Inorg. Chem.*, 1978, **17**, 1042.

Received 14*th October* 1982; *Paper* 2/1768