Inorganica Chimica Acta, *160* (1989) 245–248

Stability of the Complex of Nickel(II) with Cyclam

ANN EVERS and ROBERT D. HANCOCK*

Department of Chemistry, University of the Witwatersrand, Johannesburg 2050 (South Africa)

(Received September 5, 1988; revised January 17, 1989)

Abstract

The formation constant for the Ni(II) complex of cyclam (1,4,8,11-tetraazacyclododecane) was measured by an out-of-cell technique to be 20.1 ± 0.5 in 0.5 M NaCl at 25 °C. This is somewhat less than the value of 22.2 reported by D. Hinz and D. W. Margerum, *Inorg. Chem.*, *13* (1974) 2941. The new $\log K_1$ for Ni(II) with cyclam is more reasonable in relation to the $\log K_1$ values observed for other tetraazamacrocycle complexes of Ni(II), and also other metal ions. Possible reasons for the difference between the value for $\log K_1$ reported here and Margerum's value are discussed.

Introduction

The formation constant of the nickel(II) complex with cyclam is of particular interest because it was part of the set of complexes studied by Margerum *et al.* [1, 2] in the pioneering work which established the presence of the macrocyclic effect, a term which Margerum coined. Thus, Hinz and Margerum found [2] that $\log K_1$ for the cyclam complex of Ni(II) was 22.2, as compared with a $\log K_1$ value of only 16.4 for the complex of the open-chain polyamine analogue, 2,3,2-tet (see Fig. 1 for key to abbreviations for ligands). The approximately six orders of magnitude of extra stabilisation of the complex of the macrocycle is [1, 2] the thermodynamic macrocyclic effect, abbreviated here as $\log K(\text{MAC})$.

Since the time of Margerum's study the $\log K_1$ values for several other metal ions have been determined [3–6] for cyclam as well as other macrocycles with a variety of metal ions (Table 1). One finds generally for ligands such as 13-aneN$_4$ or 15-aneN$_4$, for example, that for all the metal ions, including Ni(II), $\log K(\text{MAC})$ is in the vicinity of three log units, and certainly is never as large as six log units (Table 2).

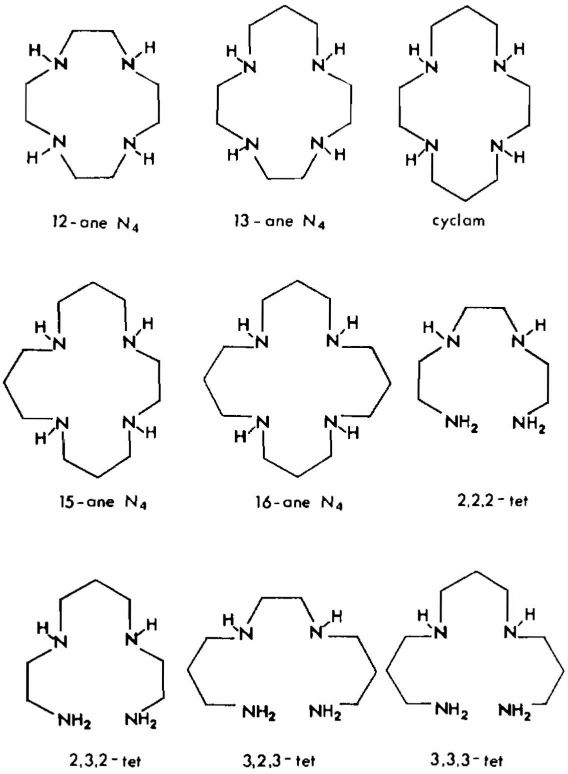

Fig. 1. Ligands discussed in this paper.

TABLE 1. Macrocyclic effect in complexes of cyclam

	Metal ion				
	Cu(II)	Ni(II)	Zn(II)	Cd(II)	Pb(II)
$\log K_1$(cyclam)	26.5	22.2	15.5	11.2	10.8
$\log K_1$(2,3,2-tet)	23.1	16.4	12.6	11.1	7.8
$\log K$(MAC)	3.4	5.8	2.9	0.1	3.0

A large variety of such evidence points to the $\log K_1$ of 22.2 for the complex of Ni(II) with cyclam being unusually large. There is no apparent reason why Ni(II) should with cyclam display such a large $\log K(\text{MAC})$, which led us to consider a redetermination of this formation constant.

A major difficulty in determining the formation constant for the complex of Ni(II) with cyclam is

---

*Author to whom correspondence should be addressed.

0020-1693/89/$3.50

TABLE 2. Macrocyclic effect in complexes of Ni(II) with tetraaza macrocycles

	Ligand			
	13-aneN_4	cyclam	15-aneN_4	16-aneN_4
log K_1(Ni)	18.0	22.2	18.4	13.2
	2,2,2-tet	2,3,2-tet	3,2,3-tet	3,3,3-tet
log K_1(Ni)	14.0	16.4	14.7	10.5
log K(MAC)	4.0	5.8	3.7	2.7

TABLE 3. Spectroscopic and pH values for the out-of-cell titration leading to a determination of log K_1 for the cyclam complex of Ni(II)[a]

Direction of equilibration[b]	[HCl]	pH	A_{450}	log K_1	
				pot.	spec.
F	8×10^{-3}	2.492	0.0366	20.03	19.64
B	8×10^{-3}	2.391	0.0347	20.78	19.93
F	6×10^{-3}	2.660	0.0547	20.07	19.68
B	6×10^{-3}	2.591	0.0527	20.51	19.84
F	5×10^{-3}	2.907	0.0866	19.50	19.79
B	5×10^{-3}	2.791	0.0766	20.03	19.84
F	4×10^{-3}	2.897	0.0882	20.51	20.00
B	4×10^{-3}	2.875	0.0942	20.72	20.26

mean log K_1: 20.3 (pot) 19.9 (spec)

overall mean: 20.1 ± 0.5

[a] In 0.5 M NaCl at 25 °C. In all solutions the total Ni concentration was 2×10^{-3} M and total cyclam was 3.2×10^{-3} M. The A_{450} for the fully formed complex was 0.1012, and for only free Ni^{2+} it was 0.004. [b] The solutions marked F were equilibrated starting with free metal ion and protonated ligand, while those marked B were equilibrated starting with the fully formed complex reacting with the acid present.

the very slow rate of equilibration of the complex-formation reaction. Margerum attempted to overcome this difficulty by studying the competition reaction between cyanide ion and cyclam for Ni(II), the equilibria involved being monitored by UV–Vis spectroscopy. In addition to the complexes $[Ni(CN)_4]^{2-}$ and $[Ni(cyclam)]^{2+}$ present in the equilibria, the complex $[Ni(cyclam)CN]^+$ had to be taken into consideration in calculating log K. A possible cause for the disagreement between the log K value determined here and that reported by Margerum, is the complexity of the equilibria involved in Margerum's determination, with, for example, the species $[Ni(cyclam)(CN)_2]$ possibly being present in considerable concentration, which was not taken into account in Margerum's calculations. A further difficulty in Margerum's approach was the fact that the Ni(II) complex of cyclam was considered to be 100% low spin, when in fact it has been shown [7] that there is an equilibrium between high- and low-spin forms present. This high-spin/low-spin equilibrium must almost certainly contribute to the disagreement between the enthalpy of complex formation determined by Margerum by measuring log K_1 as a function of temperature [2], and the enthalpy of complex formation determined calorimetrically by Paoletti *et al.* [8].

Experimental

The method chosen for determining log K_1 was an out-of-cell approach similar to that employed in several studies by us and other authors [4, 6, 9]. The basic method was that employed by us in a study of the 12-aneN_4 and 13-aneN_4 complexes of Ni(II) [3], which should be consulted for a more detailed description. In essence a set of fourteen solutions was made up, each containing the same amount of cyclam (3.2×10^{-3} M) and of nickel nitrate (2.00×10^{-3} M), but with the added HCl varying from 3×10^{-3} M to 8×10^{-3} M. Half of the solutions were duplicates, and equilibrium in pairs of duplicate solutions was approached from opposite directions, i.e. in one solution the complex was allowed to form before the acid was added, whereas in the other the acid was added to the ligand before the metal ion was added. The ionic strength of all the solutions was 0.5 M (NaCl), and the solutions were kept at 25 °C with sealed stoppers in a water bath. Periodically the spectra of the solutions were recorded so as to monitor the progress towards equilibrium. After two years (!) it was found that the rate of change had become virtually negligible, and the spectra of the pairs of duplicate solutions, approaching equilibrium from opposite directions, were tending to be the same. Inspection of Table 3 shows that even after two years full equilibrium had not been achieved, in that the log K_1 values calculated from the duplicate pairs are not the same, with those approaching equilibrium from the protonated base plus free metal ion direction being uniformly lower than those where equilibrium is being approached from the fully formed complex. The formation constant was calculated in two ways, namely, potentiometrically from the measured pH values, and spectroscopically from the spectra seen in Fig. 2. The mean value calculated spectroscopically is 19.9 ± 0.2, and from the potentiometric results log K_1 is 20.3 ± 0.4. Combining these two sets gives an overall mean log K_1 value of 20.1 ± 0.5. The fairly large standard deviation reflects to a large extent the fact that the forward and reverse equilibrated sets of points differ somewhat,

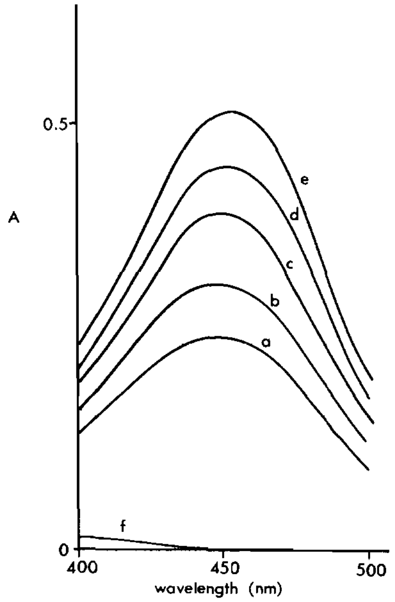

Fig. 2. Spectra of the solutions of the Ni(II) complex with cyclam after equilibrating for two years at a variety of pH values. In all of the solutions the total cyclam concentration was 3.2×10^{-3} M and the total Ni(II) was 2.0×10^{-3} M. The total acid added followed by final equilibrated pH value was for each solution: a, 8×10^{-3} M, pH = 2.391; b, 6×10^{-3} M, pH = 2.591; c, 5×10^{-3} M, pH = 2.791; d, 4×10^{-3} M, pH = 2.875; e, no added acid; f, solution of 2×10^{-3} M Ni^{2+} in 0.5 M NaCl.

being apparently not quite at equilibrium, and so bracket the mean value. A serious question which must arise after an equilibration time of two years is whether any ligand decomposition had occurred. This was addressed by taking one of the equilibrated solutions, adding sufficient Ni(II) so that the Ni:cyclam ratio was one (assuming no cyclam decomposition) and raising the pH to 6, where equilibration to form the complex is fairly rapid. The fact that a spectrum corresponding to complete formation of the expected concentration of the Ni(II)/cyclam complex was observed was taken as a strong indication that the amount of decomposition of cyclam which had occurred was insignificant. A further point is the possible presence of MLH complexes, which were found [4] to be present in the Ni(II) complexes of other tetraazamacrocycles. Analysis of the data using the program MINIQUAD [10] suggested that a small concentration of the MLH species of Ni(II) with cyclam was present, with log K for the process ML + H = MLH (M = Ni(II), L = cyclam) being 2.3 ± 0.5.

Discussion

The value of log K_1 of 20.1 ± 0.5, found here for the complex of Ni(II) with cyclam, is more in line with the expected magnitude of log K(MAC), as discussed in 'Introduction'. Thus, log K(MAC) for Ni(II) with cyclam, relative to the 2,3,2-tet complex, is 3.7 log units, similar to the three log units found for other metal ions with cyclam/2,3,2-tet, and Ni(II) with other tetraazamacrocycles, such as 13-aneN_4/2,2,2-tet or 16-aneN_4/3,3,3-tet. An interesting result of this is that now, for the macrocyclic effect, as discussed recently [11], for Ni(II) with cyclam compared to 2,3,2-tet, the macrocyclic effect is entirely an enthalpy effect, with virtually no contribution from entropy (ΔH values from ref. 8) (Table 4). This is typical of what is found for the macrocyclic effect with other metal ions [11], and it leads one to speculate whether the number of conformers available to linear polyamines as free ligands in aqueous solution was really very large. A large number of conformers for the open-chain polyamine in aqueous solution would lead to an entropy contribution to the macrocyclic effect if the macrocycle were confined to a single conformer.

A final point worth mentioning is the observed rates of equilibration of the Ni/cyclam solutions. Below a pH of 2, the rate of breakup of the Ni(II) cyclam complex becomes negligible, even after two years. As a result, sets of solutions set to equilibrate below pH 2 provided no information on the stability of the complex of Ni(II) with cyclam. Thus, $[Ni(cyclam)]^{2+}$ is kinetically stable below pH 2, and thermodynamically stable above pH 3. The kinetic stability of $[Ni(cyclam)]^{2+}$ below pH 2 possibly involves suppression of deprotonation of a coordinated nitrogen, which may be necessary to allow inversion so as to proceed with conformational changes which ultimately lead to demetallation of the macrocycle.

TABLE 4.

	ΔG(Ni(II)) (kcal mol^{-1})		ΔH(Ni(II)) (kcal mol^{-1})		ΔS(Ni(II)) (kcal mol^{-1})
Cyclam	−27.4		−24.1		11
2,3,2-tet	−21.7		−18.6		10
ΔG(MAC):	−5.7	ΔH(MAC):	−5.5	ΔS(MAC):	1

Acknowledgements

The authors thank the Council Grants Committee of the University of the Witwatersrand, and the Foundation for Research Development, for generous support for this work.

References

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

2 D. Hinz and D. W. Margerum, *Inorg. Chem., 13* (1974) 2941.

3 M. Kodama and E. Kimura, *J. Chem. Soc., Dalton Trans.,* (1977) 2269.

4 M. Micheloni, P. Paoletti and A. Sabatini, *J. Chem. Soc., Dalton Trans.,* (1983) 1189.

5 V. J. Thom, G. D. Hosken and R. D. Hancock, *Inorg. Chem., 24* (1985) 3378.

6 V. J. Thom and R. D. Hancock, *J. Chem. Soc., Dalton Trans.,* (1985) 1877.

7 A. Anichini, L. Fabbrizzi, P. Paoletti and R. M. Clay, *Inorg. Chim. Acta, 24* (1977) L21.

8 M. Micheloni, A. Sabatini and P. Paoletti, *J. Chem. Soc., Perkin Trans., 2* (1978) 828.

9 L. J. Zompa, *Inorg. Chem., 17* (1978) 2531.

10 A. Sabatini, A. Vacca and P. Gans, *Talanta, 21* (1974) 53.

11 R. D. Hancock and A. E. Martell, *Comments Inorg. Chem., 6* (1987) 237.