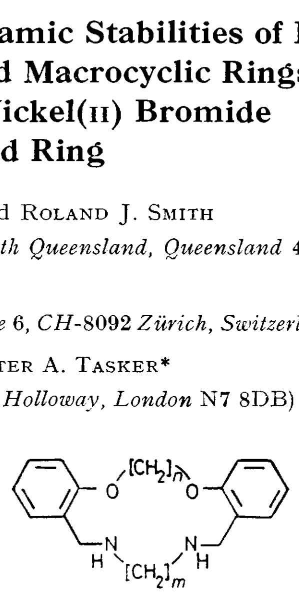
Macrocyclic Ligand Control of the Thermodynamic Stabilities of Nickel Complexes containing 14- to 17-Membered Macrocyclic Rings. *X*-Ray Crystal Structure of the *trans* Nickel(II) Bromide Complex of the 16-Membered Ring

By Kenneth R. Adam, Leonard F. Lindoy,* and Roland J. Smith
(*Department of Chemistry and Biochemistry, James Cook University of North Queensland, Queensland* 4811, *Australia*)
Giorgio Anderegg*
(*Laboratorium für Anorganische Chemie, ETHZ, Universitätstrasse* 6, *CH*-8092 *Zürich, Switzerland*)
and Kim Henrick, Mary McPartlin, and Peter A. Tasker*
(*Department of Chemistry, The Polytechnic of North London, Holloway, London* N7 8DB)

Summary The thermodynamic stabilities of 6-co-ordinate nickel complexes of related 14- to 17-membered macrocyclic ligands containing O_2N_2-donor sets show a maximum at the 16-membered ring complex; an *X*-ray structure of this complex confirms a *trans* 6-co-ordinate structure with the nickel ion contained in the hole of the ligand.

The metal-ion selectivity of macrocyclic ligands of the crown polyether or cryptate class towards non-transition metal ions has been extensively investigated.[1] Along a given series of ligands maximum stability is obtained when optimum macrocyclic ring size is reached for the particular metal ion involved. In contrast, similar macrocyclic ring size discrimination involving transition metal ions has been much less documented.[2,3]

High-spin nickel(II) complexes of the O_2N_2-donor macrocycles (**1**)—(**4**) have been characterized previously[4] and all have been assigned pseudo-octahedral geometries; such a *trans* structure was confirmed for the nickel chloride complex of (**2**) by *X*-ray diffraction.[5] Thus, unlike N_4-donor macrocyclic ligand complexes of nickel which tend to show spin-state and co-ordination number changes with variation of ring size,[2] the present complexes are ideal for comparative study of ring-size effects on the respective thermodynamic stabilities.



(**1**), $n = 2$; $m = 2$
(**2**), $n = 2$; $m = 3$
(**3**), $n = 3$; $m = 3$
(**4**), $n = 4$; $m = 3$

Protonation constants, $\beta_1 = [LH^+]/[L][H^+]$ and $\beta_2 = [LH_2^+]/[L][H^+]^2$, for ligands (**1**)—(**4**) in 95% methanol and ionic strength 0·1 M (tetramethylammonium chloride) were determined at 25 °C by the pH titration method. The following values were obtained: (**1**), log β_1 9·19, log β_2 14·59; (**2**), log β_1 9·81, log β_2 16·63; (**3**), log β_1 10·07, log β_2 17·16; (**4**), log β_1 9·56, log β_2 17·54. Stability constants for each of the nickel chloride complexes of (**1**)—(**4**) were also determined potentiometrically using the above values. Under the conditions of the study, no evidence for other than 1 : 1 ligand to metal complexation was detected. The stabilities follow the macrocyclic ring size sequence $14 < 15 < 16 > 17$ (Figure 1). This peak in stability at the 16-membered ring provides a clear example of macrocyclic ring size control of thermodynamic stability for a series of related nickel complexes. A search of the Cambridge Crystallographic Data Centre files, accessed *via* the CSSR program,[6] for nickel–ether oxygen bond distances indicated a mean (8 distances) of 2·15 Å. Since a nickel–nitrogen distance of *ca.* 2·10 Å is typical of sp^3-hybridized nitrogens in macrocyclic high-spin nickel complexes,[5] then an optimum hole size of *ca.* 4·25 Å appears reasonable for the present series. This is slightly greater than that of 4·18 Å (hole size defined as twice the mean distance of the donor atoms

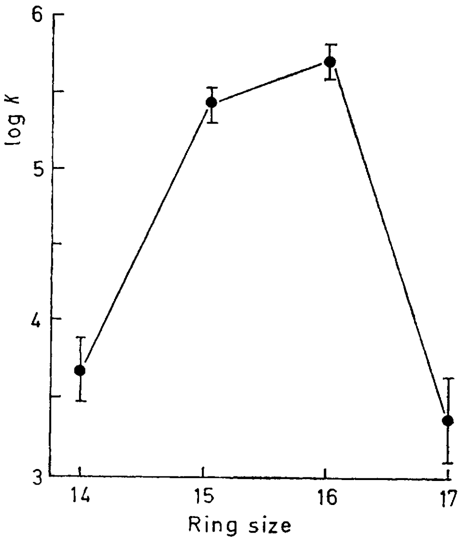


FIGURE 1. Plot of log K values *vs.* macrocyclic ring size for the nickel complexes.

from their centroid) found previously[5] for the nickel chloride complex of the 15-membered ring (**2**). X-Ray analysis of the nickel(II) bromide complex of the 16-membered ring (**3**) showed it to have a *trans*-octahedral structure (Figure 2).† Significantly, in this complex a macrocyclic hole size (see above) of 4·27 Å is obtained; this value corresponds closely to that predicted above for the hole size of optimum fit. Thus the X-ray data support the inference from the stability constant studies that, for the present series of macrocycles, the 16-membered ring provides the best fit for nickel(II) although the optimum hole size may well lie between those of the 15- and the 16-membered rings.

Crystal data: $C_{20}H_{26}Br_2N_2NiO_2$, green needles from n-butanol, M = 540·97, monoclinic, space group Cc, a = 16·835(5), b = 15·337(4), c = 8·181(2) Å, β = 95·30(2)°, Z = 4, $I/\sigma(I)>3\cdot0$, θ-range 3—30°, R = 0·046 for 1826 absorption corrected data obtained on a Philips PW1100 diffractometer with Mo-K_α radiation.

There is an almost planar 'N_2O_2' donor set presented by the macrocycle (maximum deviation of N and O atoms from the N_2O_2 plane is 0·02 Å). Important bond lengths and angles are shown with Figure 2.

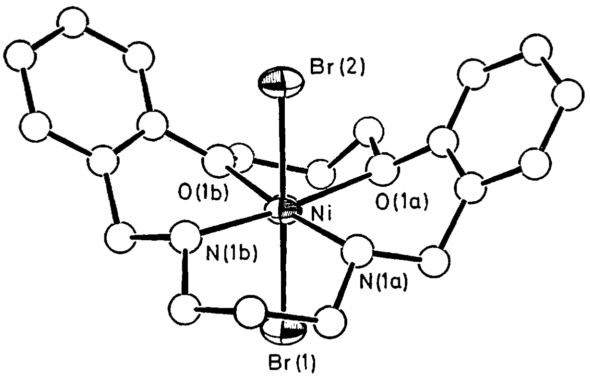


FIGURE 2. The structure of the nickel(II) bromide complex of (**3**). Bond lengths to the Ni atom (Å) are Br(1) 2·511(2), Br(2) 2·566(2), O(1a) 2·258(7), O(1b) 2·198(8), N(1a) 2·058(9), and N(1b) 2·941(9). Bond angles at the Ni atom (°) are, Br–Ni–Br 178·4; O–Ni–O 85·2; N–Ni–N 96·8; N–Ni–O 173·0, 174·1; N–Ni–O 87·8, 90·1; O(1a)–Ni–Br(1) 91·6; O(1a)–Ni–Br(2) 88·0; O(1b)–Ni–Br(1) 89·1; O(1b)–Ni–Br(2) 89·4; N(1a–Ni–Br(1) 92·0; N(1a)–Ni–Br(2) 89·5; N(1b)–Ni–Br(1) 91·8; and N(1b)–Ni–Br(2) 88·5.

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† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

[1] J. M. Lehn, *Structure and Bonding*, 1973, **16**, 1.

[2] D. H. Busch, *Accounts Chem. Res.*, 1978, **11**, 392.

[3] T. E. Jones, L. L. Zimmer, L. L. Diaddario, D. B. Rorabacher, and L. A. Ochrymowycz, *J. Amer. Chem. Soc.*, 1975, **97**, 7163; A. Anichini, L. Fabbrizzi, and P. Paoletti, *J.C.S. Dalton*, 1978, 577; M. Kodama and E. Kimura, *ibid.*, p. 1081.

[4] L. G. Armstrong, P. G. Grimsley, L. F. Lindoy, H. C. Lip, V. Norris, and R. J. Smith, *Inorg. Chem.*, 1978, **17**, 2350.

[5] A. J. Ekstrom, L. F. Lindoy, H. C. Lip, R. J. Smith, H. J. Goodwin, M. McPartlin, and P. A. Tasker, *J.C.S. Dalton*, 1979, 1027.

[6] M. Elder, P. Machin, and O. S. Mills, The Crystal Structure Search Retrieval Program, 1977, Daresbury Laboratory, Science Research Council, Daresbury, Warrington WA4 4AD.