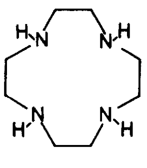
The Stability of Nickel(II) Complexes of Tetra-aza Macrocycles

Vivienne J. Thöm and Robert D. Hancock*
Department of Chemistry, University of the Witwatersrand, Johannesburg, South Africa

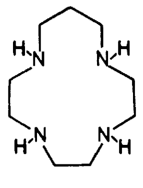
The stability constants, log K_1, have been determined by a potentiometric and u.v.-visible spectroscopic technique for the nickel(II) complexes of the tetra-aza macrocyclic ligands 1,4,7,10-tetra-azacyclododecane (L^1) and 1,4,7,10-tetra-azacyclotridecane (L^2). The value of log K_1 in 0.1 mol dm^{-3} and 25 °C was found to be 16.4 ± 0.1 for L^1 and 17.98 ± 0.05 for L^2. The variation of log K_1 for 12- to 16-membered ring tetra-aza-macrocycles as a function of metal-ion size is discussed. Two clear trends emerge. First, the larger the metal ion, the more strongly it prefers the smallest macrocycle, L^1, and secondly, the smaller the metal ion, the more it prefers to complex with the 14-membered ring L^3. This apparent paradox is explained in terms of molecular mechanics (m.m.) calculations, which show that the 12-membered macrocycle is more flexible than the 14-membered, and has effectively a larger cavity for accommodating the metal ion. A particularly puzzling feature is that low-spin nickel(II) complexes more strongly with L^3 than with L^2, even though the cavity size in L^2 is a better fit for low-spin Ni^{II} as shown by m.m. calculations and numerous crystallographic studies. Possible causes of this are discussed.

A distinctive feature of the co-ordinating properties of the crown ethers is the selectivity for metal ions which they display on the basis of the match between the size of the metal ion and the cavity in the centre of the ligand.[1] We have recently been examining this 'hole-size selectivity' in the nitrogen-donor tetra-aza macrocycles.[2] This hole size has been estimated using molecular mechanics (m.m.) calculations[3] for the ligands L^1—L^5. It increases in a monotonic fashion as the number of atoms forming the ring increases from L^1 to L^5. By analogy with the behaviour of crown ethers, we would thus expect the smallest metal ions to complex most strongly with the smaller members of the series, and the larger metal ions to complex most strongly with the larger members. When this idea is examined, however, a paradox emerges.[2] The very largest metal ions, such as Pb^{II}, complex most strongly with the smallest member, *i.e.* L^1, while smaller metal ions such as Cu^{II} prefer the macrocycles of intermediate size, such as L^3.

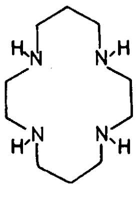
Nickel(II) is a metal ion of particular interest, since it is in a sense two metal ions in one, namely the high-spin form, exhibiting M–N bond lengths of 2.1 Å,[4] and the low-spin form with M–N lengths of 1.9 Å.[5] One should thus be able to analyse the relative stabilities of these two forms in terms of the hole-size selectivities of the ligands L^1—L^5, and the difference in size between them. The kinetic inertness of the nickel(II) complexes of these tetra-aza macrocycles presents special difficulties in determining the stabilities of the complexes. Hinz and Margerum[6] followed the competition between L^3 and cyanide ion for Ni^{II} in order to determine log K_1 (the formation constant) of the complex with L^3. More recently Micheloni *et al.*[7] used an 'out-of-cell' potentiometric titration to determine log K_1 for complexes of L^4 and L^5. In this approach, sets of solutions are made up, each solution corresponding to a single point in a normal glass-electrode potentiometric determination of stability constants.[7,8] These solutions are then allowed to come to equilibrium in a thermostatted bath, and the pH of each is measured; the formation constant is then calculated in the normal way. We have recently[2] used the same technique on the copper(II) complexes of L^1—L^3, except that the extent of complex formation as a function of pH was followed using the electronic spectra of Cu^{2+} and of the complexes formed. In order to complete our analysis of hole-size selectivity in L^1—L^5, we report here a spectroscopic study of the complexation equilibrium between L^1 and L^2 with Ni^{II}.



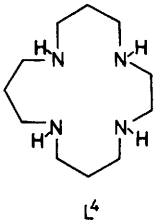
L^1



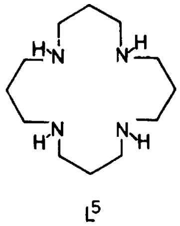
L^2



L^3



L^4



L^5

Experimental

The ligand L^1 was obtained from Parish Chemicals as the tetrahydrochloride salt. Ligand L^2 was synthesized according to the method of Fabbrizzi[5] as the hydrobromide salt. The freshly recrystallized material analysed as having 3.75 HBr per ligand molecule. On extensive drying under vacuum this dropped to 3.33 HBr. Stock solutions of the ligands were prepared, and then standardized. The required quantities of AgNO$_3$ to precipitate the halide ions were then added, and after filtration the solutions were restandardized. These stock solutions were used to make up sets of solutions which would give convenient variations in intensity of the spectra of the Ni^{2+} ion and its complex, which was roughly 10^{-2} mol dm^{-3} in nickel. It was found that a pH range from 2.00 up to about 4.00 was sufficient to produce solutions ranging from complete break-up to complete formation of the nickel(II) complexes of L^1 and L^2. Both experiments were carried out in 0.1 mol dm^{-3} NaNO$_3$. Equilibration of the sets of solutions took place over 4 weeks in a water-bath thermostatted to 25 °C, although visual inspection suggested that no change took place after the first few days. The spectra of the sets of solutions were recorded on a Cary 2300 spectrophotometer in cells thermostatted to 25 °C. The pK_a values used in calculating the log K values were from refs. 2 and

Table. Formation constants for some tetra-aza macrocycles of Ni^{II}, and the enthalpy and entropy of formation of the high- and low-spin forms

	L^1	L^2	L^3	L^4	L^5
log K_1	16.4(1)[a]	17.98(5)[a]	22.2[b]	18.38[c]	13.23[c]
ΔG° (high spin)[d]	−93.6	−97.5	−123.6	−104.9	−75.5
ΔH° (high spin)[e]	−47.8	−83.7	−100.8	−74.9	−40.6
ΔS° (high spin)[f]	154	46	77	101	117
ΔG° (low spin)[d]	*ca.* −82	−102.2	−125.9	*ca.* −94	
ΔH° (low spin)[e]		−52.3	−78.2		
ΔS° (low spin)[f]		167	160		

[a] This work, 0.1 mol dm^{-3} $NaNO_3$ and 25 °C. [b] Ionic strength 0.1 mol dm^{-3}, ref. 6. [c] Ionic strength 0.5 mol dm^{-3}, ref. 7. [d] Calculated from constants for the high-spin to low-spin equilibrium given in ref. 5. These constants are known only approximately for L^1 and L^4. [e] In kJ mol^{-1}, at $I = 0.5$ mol dm^{-3} (M. Mauro, P. Paoletti, A. Poggi, and L. Fabbrizzi, *J. Chem. Soc., Dalton Trans.*, 1982, 61). [f] In J K^{-1} mol^{-1} calculated from the ΔG° and ΔH° values assuming that ΔH° will not be much affected by differences in ionic strength.

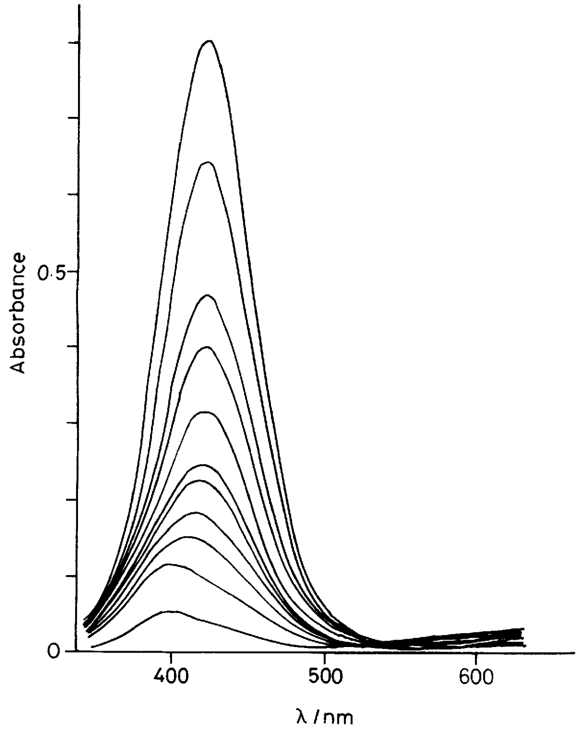


Figure 1. U.v.-visible spectra of a set of solutions used for the determination of the formation constant of Ni^{II} with 1,4,7,10-tetra-azacyclotridecane (L^2). The solutions all contain 6.0 × 10^{-3} mol dm^{-3} Ni^{2+} plus 1.05 × 10^{-2} mol dm^{-3} L^2 in 0.1 mol dm^{-3} $NaNO_3$ at 25 °C. pH values (for solutions in order of decreasing intensity at 426 nm): 2.803, 2.610, 2.492, 2.454, 2.377, 2.329, 2.231, 2.160, 2.088, and 1.925; the last solution is for 0.010 mol dm^{-3} Ni^{2+} with no L^2 present

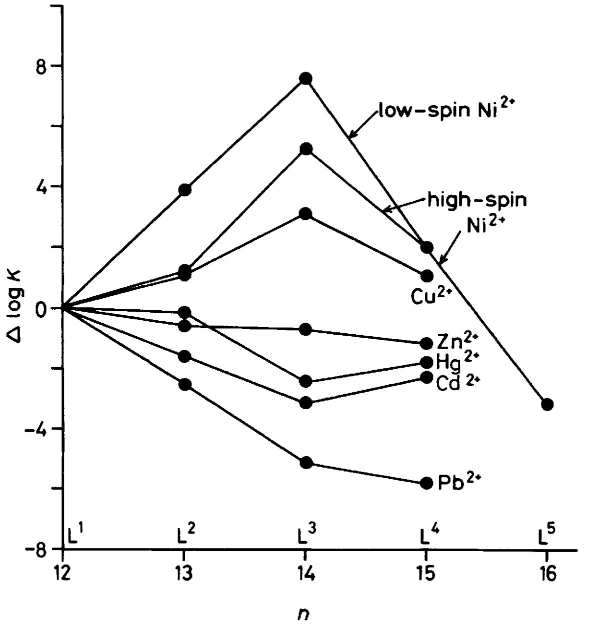
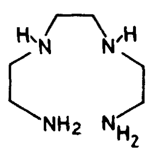


Figure 2. The effect of the size of the macrocyclic ring on the stability of the complexes formed by various metal ions with the tetra-aza macrocycles, plotted as stability relative to the stability of the complex with L^1. The value of Δ log K is thus log K_1 for the ligand indicated minus log K_1 for L^1, and n is the number of atoms forming the macrocyclic ring

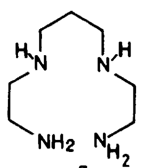
9. Figure 1 shows the electronic spectra of the set of solutions used to calculate log K_1 for the complex of L^2 with Ni^{II}.

Results and Discussion

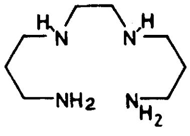
The log K_1 values for the complexes of Ni^{II} with L^1 and L^2 are shown in the Table, together with the corresponding values for L^3—L^5, as well as the stability of the high- and low-spin forms of each complex calculated using previously reported[5] constants for the high-spin to low-spin equilibrium. The trend in stability order for both spin states of Ni^{II} continues the trend found previously[2] for other metal ions, namely that large metal ions prefer the smallest macrocycle L^1, while as the size of the metal ion decreases the preference for L^3 becomes more pronounced. This behaviour (Figure 2) is simply explained[2] by the fact that the hole size in L^1 is actually *larger* than that in L^3. This rather surprising result comes about because the most stable form of L^1 as indicated[10] by m.m. calculations is the *trans*-I(+ + + +) form, which has all its nitrogens oriented so that their hydrogens are on the same side of the macrocycle. The hole size in this conformer of L^1 is such that metal ions showing M–N lengths of 2.11 Å fit best.[10] On the other hand, the hole size in L^3 in its most stable conformer, the *trans*-III(+ + − −) form, is such that metal ions with M–N bond lengths of 2.05 Å fit best. In addition, the macrocyclic ring of L^1 is much more flexible with respect to expansion and contraction, and is, in particular, able to accommodate large metal ions much more easily than can L^3. The reason for this is that the six-membered chelate rings are much less flexible with respect to expansion and contraction, because the hydrogens on these rings are able, as with cyclohexane, to assume an all-staggered position, which



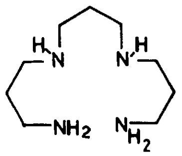
L^6



L^7



L^8



L^9

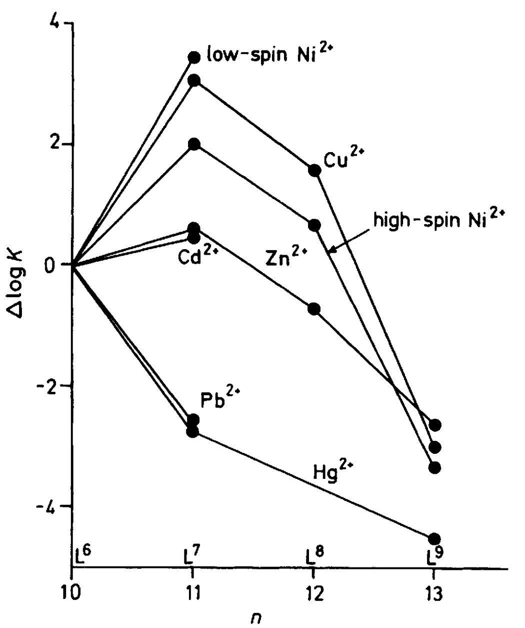


Figure 3. The effect of the size of linear open-chain tetra-aza ligands on the stability of complexes formed with various metal ions. The value of $\Delta \log K$ is thus $\log K_1$ for the ligand indicated minus $\log K_1$ for L^6, and n is the number of atoms forming the backbone of the open-chain tetra-amine. Data from R. M. Smith, and A. E. Martell, 'Critical Stability Constants,' Plenum Press, New York, 1975, vol. 2

is lost on deforming the ring. No such arrangement is possible for the five-membered rings, and we find here a low barrier to distortion.[10] The same effect is found for the open-chain tetra-aza amines L^6—L^9, as seen in Figure 3. The larger the metal ion, the more its complexes are destabilized by the presence of six-membered rings.

The high- and low-spin forms of Ni^{II} fit this pattern exceedingly well, for both the macrocyclic series L^1—L^5 and the open-chain ligands L^6—L^9. In particular, low-spin Ni^{II} with its ideal Ni–N bond length of 1.9 Å is the smallest metal ion in Figures 1 and 2 and therefore shows the greatest preference for the small cavity of the $(+ + - -)$ conformer of L^3 as compared to the larger cavity of $(+ + + +)$ L^1. All would seem logical if it were not for L^2. The m.m. calculations show that L^2 in its $(+ + - -)$ conformer has a cavity such that metal ions with M–N bond lengths of 1.92 Å fit best.[10] This is the conformer actually observed in the structure of the 3,3-dimethyl form of L^2 in its complex with low-spin Ni^{II}.[11] In accord with the best-fit hypothesis,[5,12] we find that the maximum value for the in-plane ligand-field strength, $10Dq_{xy}$, occurs for the low-spin complex of Ni^{II} with L^2. That is to say that the maximum ligand-field strength occurs for the macrocycle in the series L^1—L^5 which fits best around the metal ion.[12] There can be no doubt that L^2 fits low-spin Ni^{II} best. In the many structures reported for low-spin Ni^{II} with open-chain amines, the Ni–N bond length is always close to 1.9 Å.[5] Two additional structures in this regard are for the low-spin Ni^{II} complex co-ordinated to two ethylenediamines[13] and two *C,C,C′,C′*-tetramethylethylenediamines.[14] Here the Ni–N bond lengths are 1.92(1) and 1.91(1) Å respectively. In the low-spin complex of the methyl-substituted form of L^2 with Ni^{II} the observed Ni–N lengths are actually[11] slightly shorter than this, at 1.86(2) Å.

The problem, then, is simply that if low-spin Ni^{II} fits best into L^2, as indicated by structural studies and the electronic spectrum, why does the stability of the low-spin form not peak here? Figure 1 shows that it peaks strongly at L^3, which is too big. Other very small metal ions, such as Co^{III} and Ni^{III}, which might have been expected to show a maximum in stability at L^2, also appear[15,16] to show a maximum at L^3.

Several explanations are possible for this effect, none of them very convincing at this stage, so that we will not go into them in any great detail. One possibility is that the best fit for all these metal ions is provided by L^3, and that the high $10Dq$ encountered for the L^2 complexes is due to compression.[17] However, the very great weight of crystallographic evidence is against this.[12] Another possibility is that the differences in stability are produced by differences in the solvational or strain energies of the free ligand, *i.e.* the extent of solvent to be removed on complex formation is greater for L^2 than L^3, in accord with ideas on the origin of the macrocyclic effect,[6] or L^2 is in a very much lower state of strain than L^3. Another possibility is that steric interactions with axially co-ordinated ligands, such as solvent molecules, are greater for the complexes of L^2 than of L^3. This effect would then account for the stronger in-plane ligand field in the L^2 complexes, since these would be unaffected by unfavourable steric interactions with axially co-ordinated ligands. In support of this, crystallographic studies of L^3 complexes with *trans* ligands suggest[10] very serious steric hindrance to the axial co-ordination sites. There is, however, no evidence of any water molecules co-ordinated to the axial sites in the low-spin nickel(II) complexes. Another possible contribution is the inductive effect of the extra methylene groups in the six- as opposed to five-membered chelate ring. The importance of such inductive effects has already been discussed for simpler amines,[18] but it seems far from certain that the relatively small change of introducing a single methylene group could produce such a large change in stability. A final possibility, which may be the most important, is to be found in analyzing the *distribution* of strain in the complexes of low-spin Ni^{II} with L^2 and L^3. We have pointed out previously[12] that the ligand-field parameters, which reflect the extent of overlap in the M–L bond, are affected only by strain in the M–L bond itself, and are unaffected by strain in the rest of the complex. The strain energies calculated for the $(+ + - -)$ forms of the low-spin Ni^{II} complexes of L^2 and L^3 are rather similar, about 60 kJ mol^{-1}. However, the strain in the Ni–N bonds, comprising the sum of the Ni–N bond-length deformations, the N–Ni–N, Ni–N–C, and Ni–N–H bond-angle deformations, is 6.7 kJ mol^{-1} for the L^2 complex and very much larger at 23.0 kJ mol^{-1} for that of L^3. How this large difference in strain in the Ni–N bonds arises can be seen from inspecting the structures of the L^2 complex and of several *C*-methyl-substituted complexes of L^3 with low-spin Ni^{II}. In the latter complexes[19] the Ni–N bonds are all in the range 1.95—1.97 Å, showing that they have been stretched from the ideal length of 1.90 Å, and it is this which gives the high strain in Ni–N of 23.0 kJ mol^{-1}. In the L^2 complex the Ni–N bond lengths[11] are not distorted, but in order to orient the orbitals on the nitrogens so as to overlap with the Ni^{II} the hydrogens on the central ethylene bridge of the ligand have to adopt a completely eclipsed position,[11] which causes high strain in the ligand itself but has relatively little effect on the Ni–N bonds. Thus, low-spin Ni^{II} fits best into L^2 only insofar as the required Ni–N bond lengths are concerned, but in order to complex the strain in the rest of the ligand has to be high.

Acknowledgements

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References

1 J. D. Lamb, R. M. Izatt, J. J. Christensen, and D. J. Eatough, in 'Coordination Chemistry of Macrocyclic Compounds,' ed. G. A. Melson, Plenum Press, New York, 1979, p. 145.
2 V. J. Thöm, G. D. Hosken, and R. D. Hancock, *Inorg. Chem.*, in the press.
3 L. Y. Martin, L. J. De Hayes, L. J. Zompa, and D. H. Busch, *J. Am. Chem. Soc.*, 1974, **96**, 4047.
4 G. J. McDougall, R. D. Hancock, and J. C. A. Boeyens, *J. Chem. Soc., Dalton Trans.*, 1978, 1438.
5 L. Fabbrizzi, *J. Chem. Soc., Dalton Trans.*, 1979, 1857.
6 F. P. Hinz and D. W. Margerum, *Inorg. Chem.*, 1974, **13**, 2941.
7 M. Micheloni, P. Paoletti, and A. Sabatini, *J. Chem. Soc., Dalton Trans.*, 1983, 1189.
8 L. J. Zompa, *Inorg. Chem.*, 1978, **17**, 2531.
9 M. Kodama and E. Kimura, *J. Chem. Soc., Dalton Trans.*, 1976, 116.
10 V. J. Thom, C. C. Fox, J. C. A. Boeyens, and R. D. Hancock, *J. Am. Chem. Soc.*, 1984, **106**, 5947.
11 J. M. Waters and K. R. Whittle, *J. Inorg. Nucl. Chem.*, 1972, **34**, 155.
12 V. J. Thöm, J. C. A. Boeyens, G. J. McDougall, and R. D. Hancock, *J. Am. Chem. Soc.*, 1984, **106**, 3198.
13 R. Stomberg, *Acta Chem. Scand.*, 1969, **23**, 3498.
14 R. Alcala, J. Fernandez, F. Gomez-Beltran, and A. Larena, *Cryst. Struct. Commun.*, 1977, **6**, 635.
15 D. H. Busch, *Acc. Chem. Res.*, 1978, **11**, 392.
16 A. Bencini, L. Fabbrizzi, and A. Poggi, *Inorg. Chem.*, 1981, **20**, 2544.
17 D. H. Busch, K. Farmery, V. Goedken, V. Katovic, A. C. Melnyk, C. R. Sperati, and N. Tokel, *Adv. Chem. Ser.*, 1971, **100**, 44.
18 R. D. Hancock, B. S. Nakani, and F. Marsicano, *Inorg. Chem.*, 1983, **22**, 2531.
19 N. F. Curtis, in 'Coordination Chemistry of the Macrocyclic Compounds,' ed. G. A. Melson, Plenum Press, New York, 1979, p. 219.

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