

Molecular Mechanics Studies of the Conformation of the Macrocycle β -2,12-Dimethyl-3,7,11,17-tetra-azabicyclo[11.3.1]heptadeca-1(17),13,15-triene (L^1) in the Free State and in a Series of Nickel Complexes. Crystal and Molecular Structure of L^1 *

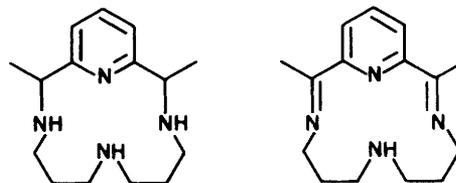
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The crystal structure of the free macrocycle β -2,12-dimethyl-3,7,11,17-tetra-azabicyclo[11.3.1]heptadeca-1(17),13,15-triene (L^1) is reported. Crystals are monoclinic, space group $P2_1/a$, with $a = 8.433(9)$, $b = 23.697(12)$, $c = 8.653(10)$ Å, $\beta = 113.9(1)^\circ$, and $Z = 4$. A total of 810 independent reflections above background have been refined to R 0.077. The free macrocycle has a folded shape very different from the conformation that is found in metal complexes. Empirical force-field methods have been used to calculate the steric energies of the various conformations of this ligand in the free state and in a series of nickel complexes, viz. $[\text{NiL}^1]^{2+}$, $[\text{NiL}^1(\text{NO}_2)(\text{ONO})]$, and $[\text{NiL}^1(\text{en})]^{2+}$ (en = ethylenediamine), and also to provide a hole-size profile for the macrocycle.

Molecular mechanics has been successfully applied to organic molecules for a number of years.¹ Recently there has been increasing interest in using force-field methods to calculate strain energies in metal complexes.²⁻⁹ The main problem in such applications is that reliable estimates of the force constants for bond lengths and angles involving the metal are hard to obtain. In organic molecules the parameters have been optimised so that the resulting refined structures fit dimensions from crystal structure analyses. However the situation is much more complicated with transition metals because of the intricacies of metal-ligand bonding and the fact that different metals prefer different co-ordination sphere geometries. It is important therefore to use the method to compare conformations of related compounds where such differences can be minimised.

Our interest in this paper is in using force-field calculations for two purposes. First we investigate the various conformations of the title ligand L^1 in the free state (1) and in a number of metal complexes whose structures have been determined by X-ray crystallography, viz. $[\text{NiL}^1]^{2+}$ (2), $[\text{NiL}^1(\text{en})]^{2+}$ (3; en = ethylenediamine), and $[\text{NiL}^1(\text{ONO})(\text{NO}_2)]$ (4). We then demonstrate that some of these conformational differences of L^1 in the various complexes are explicable by consideration of steric energy. Secondly we utilise force-field methods to calculate a hole-size profile of the macrocycle L^1 following a method described recently.⁹

L^1 is a useful macrocycle to use for these calculations as it has been shown to adopt a series of different conformations in metal complexes. The condensation of 2,6-diacetylpyridine with bis(3-aminopropyl)amine in the presence of Ni^{II} salts produces the macrocyclic complex $[\text{NiL}^3]^{2+}$ which was first isolated as the perchlorate salt.¹⁰ The trimethine unit of this macrocycle is rigid and it seems unlikely that the remaining nitrogen atom could be other than coplanar with these three nitrogens. In the one crystal structure that has been determined, namely $[\text{NiL}^3\text{Br}]\cdot\text{Br}\cdot\text{H}_2\text{O}$, the four nitrogen atoms form a square-planar environment for the metal.¹¹



L^1 (β form, *meso* Me) L^3
 L^2 (α form, *racemic* Me)

The more flexible macrocycles L^1 and L^2 can be produced by reduction of L^3 . Thus reduction of $[\text{NiL}^3]^{2+}$ under mild conditions led to two forms of the complex $[\text{NiL}^2]^{2+}$, a yellow α form (5) (containing the racemic isomer L^2), in which the two methyl groups are on opposite sites of the ring plane, and a red β form (containing the *meso* isomer L^1) in which the methyl groups are on the same side of the ring. The two forms were obtained in the α : β ratio of 1:10.

Crystal structures of both α - L^2 and β - L^1 forms of $[\text{NiL}]\cdot[\text{ClO}_4]_2$ have been determined^{12,13} and show similar square-planar structures with the maximum deviation of a contributing atom from the NiN_4 plane being *ca.* 0.11 Å. L^1 proved more flexible than L^2 and a larger range of complexes was prepared by Karn and Busch¹⁴ including $[\text{NiL}^1(\text{NO}_2)(\text{ONO})]$ (4) where the nickel environment is six-co-ordinate octahedral, but with the macrocycle providing a square-planar environment.¹⁵ The most novel compound in this series was $[\text{NiL}^1(\text{en})]^{2+}$ (3), in which the perforce *cis* arrangement of the en chelate forces the macrocycle L^1 into a very different conformation. The crystal structure¹⁶ shows that while three of the nitrogen atoms are coplanar with the metal atom, the fourth, N(14) (see Figure 1), is folded round into a perpendicular axial site.

Thus it was demonstrated that L^1 was flexible enough to vary its conformation to accommodate various other donor ligands. An additional interesting feature of this macrocycle was that it proved possible to remove the metal and prepare the free macrocycle L^1 .

We have therefore determined the crystal structure of the free macrocycle L^1 to compare its conformation with that found in the metal complexes (2), (3), and (4).

* Supplementary data available (No. SUP 56486, 5 pp.): H-atom co-ordinates, thermal parameters, least-squares planes, details of molecular mechanics calculations on isomers of L^1 . See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1986, Issue 1, pp. xvii-xx. Structure factors are available from the editorial office.

Non-S.I. units employed: dyn = 10^{-5} N, cal = 4.184 J.

Results and Discussion

The structure of L^1 (1) is shown in Figure 1 together with the atomic-numbering scheme. In order to compare the conformation of the free macrocycle (1) with that observed in the nickel complexes $[\text{NiL}^1]^{2+}$ (2) and $[\text{NiL}^1(\text{en})]^{2+}$ (3), relevant torsion angles are listed in Table 1 and in Figure 2 we show the three

Table 1. Torsion angles ($^\circ$) in compounds (1)–(5)

(a) Observed values in crystal structures*					
	(1)	(2)	(3)	(4)	(5)
N(4)–C(5)–C(9)–N(10)	–47	–24	–21	–18	–1
C(5)–C(9)–N(10)–C(11)	–65	164	141	151	125
C(19)–C(9)–N(10)–C(11)	171	–72	–91	–82	–133
C(9)–N(10)–C(11)–C(12)	179	177	–79	177	170
N(10)–C(11)–C(12)–C(13)	–88	70	–72	74	49
C(11)–C(12)–C(13)–N(14)	60	–73	74	–75	–52
C(12)–C(13)–N(14)–C(15)	178	–179	179	179	–163
C(13)–N(14)–C(15)–C(16)	69	172	–167	178	–78
N(14)–C(15)–C(16)–C(17)	49	68	–69	77	–68
C(15)–C(16)–C(17)–N(1)	51	–65	66	–72	68
C(16)–C(17)–N(1)–C(2)	176	–174	68	177	180
C(17)–N(1)–C(2)–C(3)	62	–153	–161	–160	161
C(17)–N(1)–C(2)–C(18)	–173	79	70	82	–78
N(1)–C(2)–C(3)–N(4)	41	20	32	26	–19

(b) Values obtained in molecular mechanics calculations					
N(4)–C(5)–C(9)–N(10)	–51	–12	4	–12	12
C(5)–C(9)–N(10)–C(11)	–65	151	126	143	103
C(19)–C(9)–N(10)–C(11)	174	–85	–111	–91	–137
C(9)–N(10)–C(11)–C(12)	176	170	–70	175	173
N(10)–C(11)–C(12)–C(13)	–84	72	–76	76	53
C(11)–C(12)–C(13)–N(14)	61	–69	74	–74	–54
C(12)–C(13)–N(14)–C(15)	177	180	–179	178	160
C(13)–N(14)–C(15)–C(16)	65	173	–171	–177	–73
N(14)–C(15)–C(16)–C(17)	48	68	–70	74	–67
C(15)–C(16)–C(17)–N(1)	55	–69	67	–76	67
C(16)–C(17)–N(1)–C(2)	177	–167	70	–176	173
C(17)–N(1)–C(2)–C(3)	61	–142	–138	–146	148
C(17)–N(1)–C(2)–C(18)	–177	94	98	89	–88
N(1)–C(2)–C(3)–N(4)	44	07	03	14	–12

* Standard deviations are 1° . As all five unit cells are centrosymmetric the signs of any one structure can be reversed. Also because of the nature of the macrocycle there are two alternative numbering schemes, N(1), C(2), ... N(10) etc., could be N(10), C(9), ... N(1) etc.

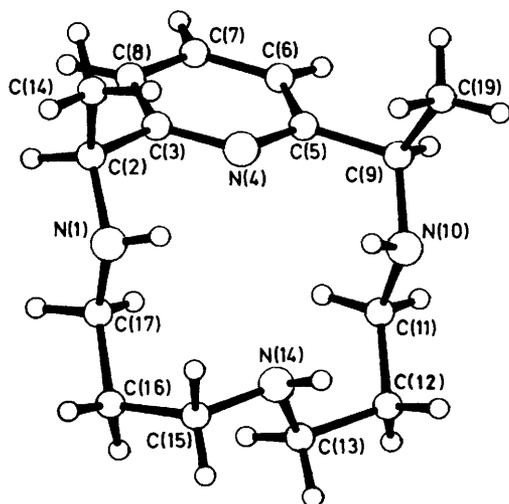


Figure 1. The structure of L^1 (1)

different conformations for L^1 with projections down the N(1) ... N(10) vector for (1), (2), and (3).

In the free macrocycle the four nitrogen atoms are closely planar with the maximum deviation of an atom from the N_4 plane being 0.08 Å. Despite this planarity, it is clear, particularly from Figure 2(a) that the remainder of the macrocycle atoms deviate considerably from this plane, a geometry unlike that found in the predominantly planar complex $[\text{NiL}^1]^{2+}$ (2) [Figure 2(b)]. In (1) the macrocycle is folded so that all atoms with the exception of C(2), C(9), and C(15) (respective distances 0.03, –0.14, and –0.02 Å) and the methyl groups C(18), C(19) are on the positive side of the N_4 plane [see Figure 2(a)]. Least-squares plane deviations are given in SUP 56486.

In (1) the four close N ... N distances [N(1) ... N(4) 2.82(2), N(4) ... N(10) 2.87(2), N(10) ... N(14) 3.12(2), and N(1) ... N(14) 3.29(2) Å] are considerably larger than the respective values in the nickel complexes, viz. 2.53, 2.51, 2.86, 2.92 Å in (2); 2.66, 2.65, 2.99, 3.16 Å in (3); and 2.66, 2.62, 3.13, 3.13 Å in (4). These distances are of two types, those involving the pyridine nitrogen atom N(4) (type A) and those involving N(14) (type B).

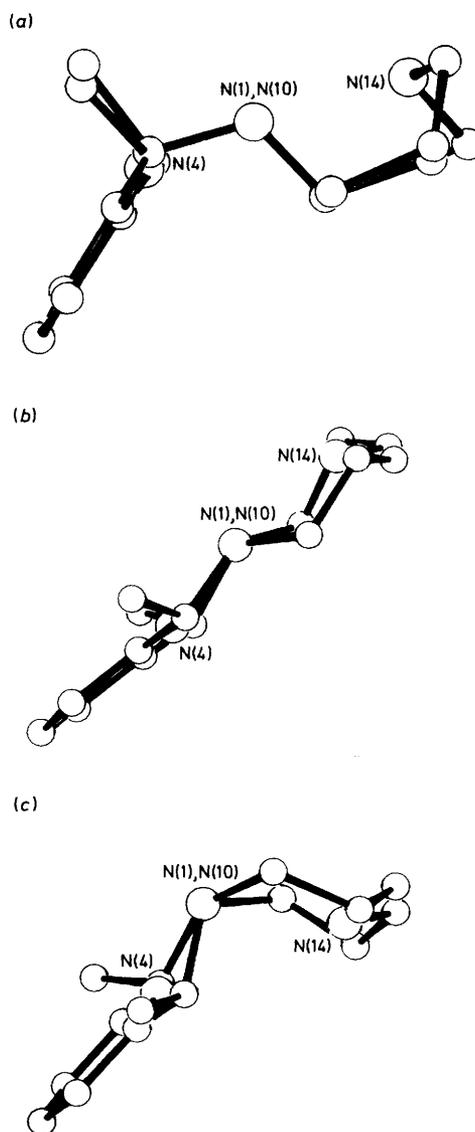


Figure 2. Projection of structures (1), (2), and (3) onto the N(1) ... N(10) vector: (a) L^1 (1), (b) $[\text{NiL}^1]^{2+}$ (2), and (c) $[\text{NiL}^1(\text{en})]^{2+}$ (3)

Mean values in (1) are both considerably larger than those in (2) and (3), *viz.* for type A 2.84 (1) *vs.* 2.52 (2), 2.65 (3), 2.64 Å (4), and for type B 3.20 (1) *vs.* 2.89 (2), 3.08 (3), 3.13 Å (4).

Thus the presence of the metal atom not only changes the shape of the macrocycle but it also changes the size of the macrocycle hole. This emphasises the problem of calculating the hole size of a macrocycle and trying to predict whether a particular metal can be encapsulated, as clearly the hole size of L^1 varies considerably from one complex to another. It is therefore rash to calculate the hole size of a macrocycle taking the co-ordinates from just one crystal structure.^{17,18} It is necessary to consider how the macrocycle would adapt to accommodate a particular metal ion.

It seems likely that the conformation of the free macrocycle L^1 is the low-energy form and that the conformation in the metal complexes is an adjustment due to the metal co-ordination. In (1) the pyridine ring is tilted to make an angle of 49.2° with the N_4 plane. This compares to an angle of -7.9° in (2) and an angle of -16.1° between the pyridine ring and the N_4 plane in (4). In the nickel complexes the pyridine ring is approximately planar in order to facilitate N-M bonding.

Torsion angles are a useful indication of strain in a particular macrocycle conformation. Those in (1) are for the most part close to the expected 60 or 180°. In particular we note that N(4)-C(5)-C(9)-N(10) and N(1)-C(2)-C(3)-N(4) are -47 and 41°, values which are less strained than the *ca.* 25° in the metal complexes. Not only are the pyridine ring positions different in the three structures but the C(17)-N(1)-C(2)-C(18) and C(19)-C(9)-N(10)-C(11) torsion angles are close to 180° in (1) rather than 60° as found in (2) and (3).

Force-field Calculations.—We have attempted to quantify the above observations on the various conformations of L^1 by the use of force-field calculations using our version of the MM2 program.^{19,*} The parameters for N, C, and H are well established from work on organic molecules and values appropriate to the MM2 program were used.^{19,21,22} First the crystal-structure co-ordinates of (1) were input to MM2 and the structure was refined. There was relatively good agreement between observed and calculated co-ordinates (torsion angles shown in Table 1 and bond lengths and angles in Table 2). The resultant steric energy was 7.55 kcal mol⁻¹. There are two possible positions for each hydrogen atom bonded to nitrogen giving eight possible isomers in all. These structures were all refined and gave minima which had steric energies between 2.99 and 10.55 kcal mol⁻¹. Results are listed in SUP 56486. These significant variations in energy between isomers were due primarily to dipole interactions involving the N(10) lone pair (l.p.) of the type N(10)-l.p./C(3)-N(4) and N(10)-l.p./C(5)-N(4) which were very dependent upon the conformation and varied considerably from one structure to another.

There were two pairs of optical isomers among the eight conformations but these refined to slightly different energies (differences less than 0.6 kcal mol⁻¹); a result which indicates that there are at least two false minima among the eight. This result is not surprising in view of the flexibility of the 14-membered ring in the macrocycle and indeed it is to be expected that inversion about the nitrogen atoms would be facile and thus that isomers based on different N-H positions will interconvert reasonably rapidly. For a structure of this nature

* Most previous molecular mechanics calculations on transition-metal complexes have used a simple four-term force field⁷ together with Boyd's Newton-Raphson minimisation procedure.²⁰ However in this work, Allinger's MM2 force field has been used throughout. This program has achieved a much higher degree of agreement for organic molecules and is therefore more likely to provide a suitable force field for macrocyclic molecules.

Table 2. Molecular dimensions in the crystal structure of L^1 (1) compared to those obtained from molecular mechanics (MM) calculation; distances in Å, angles in °

	Crystal structure	MM Calculation
N(1)-C(2)	1.457(10)	1.465
N(1)-C(17)	1.450(12)	1.463
C(2)-C(3)	1.557(10)	1.516
C(2)-C(18)	1.495(11)	1.538
C(3)-N(4)	1.318(9)	1.308
C(3)-C(8)	1.381(11)	1.399
N(4)-C(5)	1.351(9)	1.308
C(5)-C(6)	1.387(11)	1.399
C(5)-C(9)	1.501(11)	1.516
C(6)-C(7)	1.334(14)	1.395
C(7)-C(8)	1.388(13)	1.395
C(9)-N(10)	1.477(11)	1.465
C(9)-C(19)	1.517(12)	1.538
N(10)-C(11)	1.438(12)	1.464
C(11)-C(12)	1.516(14)	1.540
C(12)-C(13)	1.553(14)	1.540
C(13)-N(14)	1.440(12)	1.460
N(14)-C(15)	1.466(11)	1.462
C(15)-C(16)	1.508(13)	1.539
C(16)-C(17)	1.526(13)	1.540
	Crystal structure	MM Calculation
C(2)-N(1)-C(17)	115.0(7)	113.3
N(1)-C(2)-C(3)	113.5(6)	112.2
N(1)-C(2)-C(18)	110.8(7)	109.3
C(3)-C(2)-C(18)	110.5(6)	109.1
C(2)-C(3)-N(4)	114.0(6)	120.1
C(2)-C(3)-C(8)	124.0(8)	121.1
N(4)-C(3)-C(8)	122.1(7)	118.8
C(3)-N(4)-C(5)	118.6(6)	125.3
N(4)-C(5)-C(6)	120.9(8)	118.9
N(4)-C(5)-C(9)	115.5(6)	119.6
C(6)-C(5)-C(9)	123.6(8)	121.4
C(5)-C(6)-C(7)	120.9(9)	119.2
C(6)-C(7)-C(8)	117.9(9)	118.4
C(3)-C(8)-C(7)	119.6(9)	119.3
C(5)-C(9)-N(10)	113.5(7)	111.5
C(5)-C(9)-C(19)	110.9(7)	109.1
N(10)-C(9)-C(19)	109.7(8)	109.3
C(9)-N(10)-C(11)	116.6(8)	113.1
N(10)-C(11)-C(12)	112.5(9)	112.4
C(11)-C(12)-C(13)	112.4(9)	114.2
C(12)-C(13)-N(14)	112.2(9)	112.4
C(13)-N(14)-C(15)	113.2(8)	114.0
N(14)-C(15)-C(16)	113.0(8)	114.5
C(15)-C(16)-C(17)	114.5(8)	114.5
N(1)-C(17)-C(16)	112.3(9)	112.0

one might expect a broad continuum of energy with many shallow minima rather than eight distinct minima representing differences in N-H positions.

The conformation of L^1 found in the crystal structure with an energy of 7.55 kcal mol⁻¹ has by no means the lowest energy and it may well be that the present isomer is stabilised by packing forces in the crystal structure. However it is clear that this conformation of the ligand, with the pyridine ring tilted by 49.2° from the N_4 plane, is considerably more stable in the absence of a metal than the more planar conformation described below where the steric energy ranges from 11.13 to 13.97 kcal mol⁻¹.

We then turned our attention to the metal complexes of L^1 . The presence of a metal atom in the centre of the macrocycle forces the macrocycle into distinct conformations and fortunately the problem of false minima is unimportant. Some values for the constants of Ni^{II} have been given,⁷ *viz.* $r_o(\text{Ni-N}) =$

2.10 Å, $k_s(\text{Ni-N}) = 0.68 \text{ m dyn } \text{Å}^{-1}$, and $k_b(\text{N-Ni-N}) = 0.30 \text{ m dyn } \text{Å rad}^{-2}$; van der Waals parameters for nickel were estimated as $r^* = 2.30 \text{ Å}$ and $\epsilon(\text{Ni}) = 0.170 \text{ kcal mol}^{-1}$ from values given for other elements in ref. 22. (Terms are defined in ref. 1.) In the first stage of the calculation, these parameters were input together with the co-ordinates of the crystal structures for (2), (3), (4), and $[\text{NiL}^2]^{2+}$ (5) which were then refined. The resulting dimensions are shown in Table 3 and show relatively poor agreement between values observed and calculated. We then optimised the nickel parameters to get the best possible fit and found that values of $k_s(\text{Ni-N}) = 2.00 \text{ m dyn } \text{Å}^{-1}$ * and $r_o = 1.86 \text{ Å}$ for low-spin (square planar) and 2.09 Å for high-spin (octahedral) were required. All other parameters were the same; indeed we found that variations of $k_b(\text{N-Ni-N})$ by factors of 100 led only to a maximum change of 0.05 Å in bond length. Large variations in r^* and ϵ also gave negligible bond length changes.

The dimensions obtained from the molecular mechanics calculations for structures (1)–(5) inclusive show reasonable agreement with crystal structure values and these are compared in Table 1 (torsion angles) and Table 3 (metal co-ordination sphere). As might be expected there was good agreement between other bond lengths and angles and therefore these are not listed here.

Only one value of the ideal bond length of r_o was included for a particular structure to account for M–N(py) (py = pyridine) and M–N(amine) bonds. As shown in Table 3 the M–N(py) bond length decreased and the M–N(amine) bond length increased from the ideal bond lengths in the refinement to approximate to the experimentally observed dimensions in the crystal structure. The crystal structure was therefore fitted without recourse to different values of r_o for M–N(py) and M–N(amine) bonds. It can be concluded from this result that the observed variations in M–N(py) and M–N(amine) bond lengths are a necessary consequence of the geometrical arrangement of the macrocycle around the metal rather than any intrinsic difference in bond strength between metal to pyridine and metal to amine bonds.

It is interesting that $[\text{NiL}^2]^{2+}$ (5) is more stable than $[\text{NiL}^1]^{2+}$ (2) by ca. $3.9 \text{ kcal mol}^{-1}$. This indicates that the ratio of 1:10 obtained for the α and β isomers during the reduction of L^3 is not due to the relative stabilities of the products but must be of kinetic origin.

We then investigated some other experimental results concerning the chemistry of L^1 . The nickel atom in (4) is bonded to two nitrite groups, one through nitrogen and one through oxygen. It was originally suggested¹⁵ that this was a steric effect. Using the crystallographic co-ordinates for (4) as a starting set we estimated co-ordinates for the dinitro- and dinitro-structures. Parameters used for the $-\text{NO}_2$ group were taken from the MM2 program. Values of r_o for the Ni–N and Ni–O bonds were set at 2.11 and 2.09 Å respectively, equivalent to crystal structure values. Values used for Ni–N–O were $k_b = 0.5 \text{ m dyn } \text{Å rad}^{-2}$, $\theta_o = 121.8^\circ$ and for Ni–O–N $k_b = 0.35 \text{ m dyn } \text{Å rad}^{-2}$, $\theta_o = 123.8^\circ$.

The co-ordinates were then refined using MM2 to give steric energies of 13.97 , 14.41 , and $13.67 \text{ kcal mol}^{-1}$ for O,N-, N,N-, and O,O-bonding respectively. These values show that the steric energy differences between O and N bonding are very small and that other factors are important in the preparation of (4). A feature of the MM2 program is that bond dipoles can be included. We assumed that the Ni–O dipole was greater than

* This value of $k_s(\text{Ni-N})$ is considerably larger than the spectroscopic force constant, $0.68 \text{ m dyn } \text{Å}^{-1}$,²³ and also values used in other force fields.⁷ We are not concerned that the value required in MM2 is so high. Parameters often vary from one force field to another and generally are not transferable.

Table 3. Results of force-field calculations for the metal co-ordination spheres compared to those obtained in crystal structures

(a) Crystal values (distances in Å, angles in °)				
	(5)	(2)	(3)	(4)
Ni–N(1)	1.90	1.95	2.16	2.08
Ni–N(4)	1.84	1.82	2.01	1.97
Ni–N(10)	1.90	1.95	2.16	2.08
Ni–N(14)	1.88	1.95	2.13	2.05
N(1)–Ni–N(4)	83.9	83.5	78.8	80.6
N(1)–Ni–N(10)	162.1	163.1	158.1	160.3
N(1)–Ni–N(14)	101.8	94.4	88.5	98.7
N(4)–Ni–N(10)	86.3	84.5	79.3	82.2
N(4)–Ni–N(14)	172.3	177.5	98.1	178.8
N(10)–Ni–N(14)	89.4	97.2	94.7	98.7
(b) Molecular mechanics results using published parameters for Ni (viz. $r_o = 2.10 \text{ Å}$, $k_s = 0.68 \text{ m dyn } \text{Å}^{-1}$, $k_b(\text{N-Ni-N}) 0.30 \text{ m dyn } \text{Å rad}^{-2}$)				
	(5)	(2)	(3)	(4)
Ni–N(1)	2.06	2.09	2.14	2.10
Ni–N(4)	1.86	1.90	1.93	1.92
Ni–N(10)	2.06	2.10	2.15	2.10
Ni–N(14)	2.08	2.13	2.27	2.16
N(1)–Ni–N(4)	84.2	84.3	82.8	83.6
N(1)–Ni–N(10)	161.2	160.8	165.1	164.6
N(1)–Ni–N(14)	99.4	94.9	90.7	96.6
N(4)–Ni–N(10)	86.3	83.1	82.9	83.6
N(4)–Ni–N(14)	175.5	178.5	93.2	176.4
N(10)–Ni–N(14)	89.5	97.4	94.3	96.6
(c) Molecular mechanics results using optimised parameters for Ni ($r_o = 1.86 \text{ Å}$ (low spin) for (2) and (5), 2.09 Å (high spin) for (3) and (4), $k_s = 2.00 \text{ m dyn } \text{Å}^{-1}$, $k_b = 0.30 \text{ m dyn } \text{Å rad}^{-2}$)				
	(5)	(2)	(3)	(4)
Ni–N(1)	1.91	1.93	2.11	2.09
Ni–N(4)	1.81	1.84	1.99	1.97
Ni–N(10)	1.91	1.94	2.12	2.08
Ni–N(14)	1.90	1.96	2.14	2.05
N(1)–Ni–N(4)	85.9	84.8	81.9	82.4
N(1)–Ni–N(10)	163.8	161.6	163.1	160.6
N(1)–Ni–N(14)	98.5	94.2	91.4	98.1
N(4)–Ni–N(10)	87.2	84.1	82.2	82.4
N(4)–Ni–N(14)	174.7	178.4	94.0	176.4
N(10)–Ni–N(14)	87.8	96.6	95.2	97.7
$E/\text{kcal mol}^{-1}$	11.53	15.41	11.13	13.97

the Ni–N dipole and included various values for the dipole in the calculation. In all cases, there was an increased difference between the three steric energies but the order remained the same, i.e. O,O < O,N < N,N.

Curry and Busch¹⁰ found that the α form, L^2 , did not give rise to either an en or nitrite complex. Trial co-ordinates for these postulated structures were calculated from the L^1 structures by changing hydrogen positions for methyl groups and *vice versa*. The refined energies of the α form of (3), viz. $[\text{NiL}^2(\text{en})]^{2+}$, are 14.56 (or $16.87 \text{ kcal mol}^{-1}$, there are two possible isomers) compared to $11.13 \text{ kcal mol}^{-1}$ for $[\text{NiL}^1(\text{en})]^{2+}$ (3). The increased energy is primarily made up of the bending terms at C(2) and van der Waals contacts involving H(1) and H(2). This result suggests that the non-formation of the α en complex has a steric origin.

The α analogues of (4), $[\text{NiL}^2(\text{NO}_2)(\text{ONO})]$ have energies of 14.87 and $14.63 \text{ kcal mol}^{-1}$ compared to $13.97 \text{ kcal mol}^{-1}$ for (4). This is due to a general increase in bending strain [especially at N(1)] but the torsional strain decreases. The van der Waals contacts are similar for the L^1 and L^2 structures.

We also calculated the hole-size profile for the α and β forms (Figure 2) of the macrocycle using our published method⁹ in which k_s , the stretching force constant for the metal–ligand

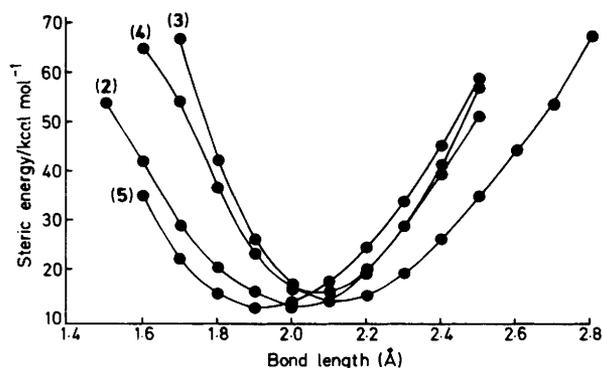


Figure 3. Plot of steric energy (kcal mol^{-1}) against M-N distance (\AA) for various L^1 and L^2 macrocycle conformations with: (2), a square-planar donor set for the L^1 macrocycle; (3), a donor set for the L^1 macrocycle based on the conformation in the $[\text{NiL}^1(\text{en})]^{2+}$ structure (the en ligand is included in the calculation); (4), a square-planar donor set for the L^1 macrocycle but with axial NO_2 and ONO groups included; and (5), a square-planar donor set for the L^2 macrocycle

bond, is increased by a factor of 10. The M-N bond length is then optimised at the expense of all other terms and the macrocycle conformation is thus forced to take up the geometry best suited to this M-N bond length, this process avoiding the problem of local minima. The values of the ideal bond length are then varied and the steric energy E is determined each time. The resulting plot of M-L vs. E (Figure 3) gives the hole-size profile for the macrocycle. Results show that L^2 has a minimum at M-L 1.90 \AA compared to 2.03 \AA for L^1 . The presence of axial ligands make little difference to the profile of L^1 but the minimum value is increased to 2.08 \AA . This is primarily due to van der Waals interactions between the axial ligands and the macrocycle. Clearly only a small but significant part (*ca.* 0.05 \AA) of the observed increase in the Ni-N bond length from low-spin square planar to high-spin octahedral as observed in the crystal structures of (2) and (4) can be ascribed to steric effects. The predominant factor in the 0.15 \AA increase is electronic.

When the macrocycle is in its folded form as in $[\text{NiL}^1(\text{en})]^{2+}$ (3), the minimum-energy bond length is increased to 2.10 \AA . This conformation is more suited than the planar form to metals with larger radii than nickel.

In this method for the calculation of a hole-size profile the macrocycle is forced [by the increased value of $k_s(\text{M-N})$] to adopt a conformation to suit a particular bond length. Other published methods either use the crystal structure co-ordinates unchanged^{17,18} or vary the bond length without allowing for changes in the macrocycle conformation in this way.^{3,4} Another method²⁴ has appeared in the literature in which the M-N stretching force constant was set to zero so that in theory the bond length would be determined only by the conformation of the macrocycle. Other parameters for the metal were kept unchanged. This method ignores the fact that there will be van der Waals interactions between the metal and nitrogen atoms, these normally being assumed to be accounted for in the bond stretching term and takes no account of possible changes in the macrocycle conformation.

Conclusions

We have shown how force-field methods can be applied to a series of experimental observations concerning the metal complexes of L^1 and L^2 . Results show that the folded conformation of L^1 in the free state has a considerably lower steric energy than the planar conformations found in nickel complexes. We also show that steric effects are responsible for

Table 4. Atomic co-ordinates ($\times 10^4$) with estimated standard deviations in parentheses for L^1 (1)

Atom	x	y	z
N(1)	-4 261(10)	858(4)	-1 425(10)
C(2)	-3 892(10)	657(4)	-2 836(11)
C(3)	-1 995(9)	772(4)	-2 617(10)
N(4)	-1 406(7)	1 274(3)	-1 990(8)
C(5)	225(10)	1 417(3)	-1 760(10)
C(6)	1 256(14)	1 048(5)	-2 191(13)
C(7)	663(14)	542(5)	-2 848(14)
C(8)	-1 012(14)	396(4)	-3 076(11)
C(9)	810(12)	1 992(4)	-1 021(12)
N(10)	430(12)	2 114(3)	468(10)
C(11)	1 308(14)	1 772(5)	1 941(14)
C(12)	816(16)	1 926(5)	3 390(15)
C(13)	-804(13)	1 598(6)	3 325(15)
N(14)	-2 312(10)	1 709(4)	1 795(10)
C(15)	-3 875(13)	1 422(4)	1 738(15)
C(16)	-3 793(16)	790(4)	1 580(14)
C(17)	-3 249(16)	593(5)	188(14)
C(18)	-5 151(12)	898(5)	-4 467(11)
C(19)	27(13)	2 448(4)	-2 343(12)

some of the chemistry of these ligands but that kinetic effects are often more important.

Calculation of the hole-size profiles of L^1 and L^2 indicate that relatively rigid macrocycles can accommodate a wide range of size of metal ion by varying their conformation.

Experimental

Preparation of L^1 (1).—The macrocycle L^1 was synthesized following the method of ref. 14 and recrystallised from a dichloromethane-light petroleum (b.p. 40–60 $^\circ\text{C}$) mixture. Crystals were eventually obtained by slow sublimation of the pure microcrystalline product in a sealed Pyrex ampoule under vacuum.

Crystallography.—*Crystal data.* $\text{C}_{15}\text{H}_{26}\text{N}_4$, $M = 262.4$, monoclinic, $a = 8.433(9)$, $b = 23.697(12)$, $c = 8.653(10)$ \AA , $\beta = 113.9(1)^\circ$, $U = 1 581.0$ \AA^3 , $Z = 4$, $D_c = 1.10$ g cm^{-3} , $\lambda(\text{Mo-K}\alpha) = 0.7107$ \AA , $\mu = 0.73$ cm^{-1} . Space group $P2_1/a$ from systematic absences $h0l$, $h = 2n + 1, 0k0$, $k = 2n + 1$. A crystal of approximate size $0.7 \times 0.25 \times 0.25$ mm was mounted on a Stoe STADI2 diffractometer and intensity data were collected via a variable width ω scan. Background counts were 20 s and a scan rate of $0.033^\circ \text{s}^{-1}$ was applied to a width of $1.5 + \sin\mu/\tan\theta$.

The maximum 2θ value was 40° . 1 246 Independent reflections were measured of which 810 with $I > 2\sigma(I)$ were included in subsequent calculations. The structure was determined using direct methods via SHELX76.²⁴ The weighting scheme was chosen to give equivalent values of $w\Delta^2$ over ranges of F_o and $\sin\theta/\lambda$. This was $w = 1/[\sigma^2(F) + 0.003 F^2]$ where $\sigma(F)$ was taken from counting statistics. All atoms were refined anisotropically. Hydrogen atoms were refined isotropically apart from those in methyl groups which were refined as rigid groups with a common thermal parameter. There are two possible positions for each of the three hydrogen atoms bonded to nitrogen atoms; all three were located in a difference Fourier and allowed to refine independently. Scattering factors were taken from ref. 25. Calculations were made using SHELX76 on the CDC7600 computer at the University of Manchester Computer Centre. The final R value was 0.077 (R' 0.075). Atomic co-ordinates are given in Table 4, molecular dimensions in Table 2.

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