The Relative Stabilities of the *R,S,S,R, R,S,R,R,* and *R,S,R,S* Isomers of Four-, Five-, and Six-Co-ordinate (1,4,8,11-Tetramethyl-1,4,8,11-tetra-azacyclotetradecane)nickel(II) Solvento Ions as Determined by Strain Energy Minimization Calculations

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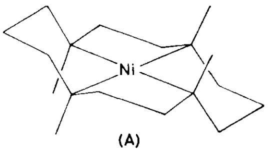
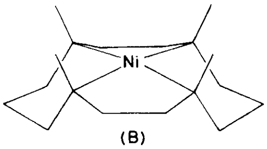
Molecular mechanical strain energy calculations suggest that, contrary to common belief, the *R,S,R,S* and *R,S,R,R* isomers of the (1,4,8,11-tetramethyl-1,4,8,11-tetra-azacyclotetradecane)nickel(II) cation are thermodynamically more stable than the *R,S,S,R* isomer; however, on addition of one or two solvent molecules to the complex, the relative stability of the *R,S,S,R* isomer increases substantially.

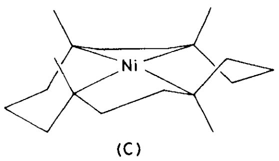
Two isomers of (1,4,8,11-tetramethyl-1,4,8,11-tetra-azacyclotetradecane)nickel(II), $[Ni(TMC)]^{2+}$, are well known; the *R,S,R,S* isomer (B) is obtained from the reaction of TMC with $[Ni(H_2O)_6]^{2+}$ in aqueous ethanol,[1] while the *R,S,S,R* isomer (A) is formed by *N*-methylation of *R,S,S,R*-$[Ni(cyclam)]^{2+}$.[2] It has long been assumed that the latter isomer, (A), is the thermodynamically more stable and that (B) is the product of a low energy kinetic pathway.[3—5] This assumption is apparently supported by the observation that (B) is unstable in acid solution while (A) is quite stable[3,4] and by the formation of (A) from the *N*-methylation of $[Ni(cyclam)]^{2+}$ which, it is claimed, should yield the thermodynamically preferred product.[4,5] It was also generally believed that the two isomers could not be interconverted; however, Moore *et al.* have shown recently that (A) and (B) interconvert easily in the presence of strongly co-ordinating solvents and apparently do so *via* the intermediate structure (C).[6] Also, Lincoln *et al.* have recently reported the observation of the *R,S,R,R* isomer (C), in the preparation of $[Ni(TMC)]^{2+}$ and its ready isomerization to the *R,S,R,S* isomer in $MeNO_2$.[7] Along with the report that free TMC adopts the *R,S,S,R* (A) geometry,[8] these observations cast doubt on the suggestion that (B) only occurs because it is kinetically preferred and is unable to convert into a more stable geometry.



(A)



(B)



(C)

In order to determine the relative stabilities of the isomers we have calculated the minimized strain energies of isomers (A), (B), and (C) of $[Ni(TMC)]^{2+}$ and of the five- and six-co-ordinate complexes obtained by the addition of isolated nitrogen atoms in the axial sites. The use of isolated nitrogen atoms as axial ligands leads to an artificial situation, but should yield results of more general applicability than use of any given ligand would. Strain energies were determined by the molecular mechanics method using a force field derived from one described previously,[9] with non-bonded interaction potentials taken from Allinger's MM2 force field,[10] and with the nickel–nitrogen bond deformation force constant used previously by McDougall *et al.*[11] The total energy is described by the sum of bond length, valence angle, and torsion angle deformation terms and non-bonded interaction energies. Minimization of the energy was achieved using the Newton–Raphson method described by Boyd.[12]

In modelling four-co-ordinate nickel(II) complexes a decision must be made as to what, if any, constraints should be applied to preserve co-planarity of the nickel and nitrogen donor atoms. No constraints were employed in the present study, and this model has successfully reproduced[13] the out-of-plane distortions observed in the related complex *R,S,R,S*-(1,4,7,10-tetramethyl-1,4,7,10-tetra-azacyclododecane)nickel(II)$^{2+}$.[14]

Minimized strain energies for all isomers are listed in Table 1. The results for the four-co-ordinate complexes show that the *R,S,R,S* isomer is the most stable and the *R,S,S,R* the least. In an equilibrium mixture at 291 K the *R,S,R,S* : *R,S,R,R* : *R,S,S,R* proportions would be 81 : 17 : 2.

Table 1. Minimized strain energies and predicted isomer proportions.

	(A)	(B)[a]	(C)[a]
4-Co-ordinate			
Strain energy (kJ mol^{-1})	141.7	131.3	135.0
Relative H (kJ mol^{-1})	10.4	0.0	3.7
Expected isomer proportions at 291 K (%)	1.1	81.3	17.6
5-Co-ordinate			
Strain energy	155.4	156.5(t)	160.2(c)
		159.9(c)	169.4(t)
Relative H	0.0	1.1(t)	4.8(c)
		4.1(c)	14.0(t)
Expected isomer proportions at 350 K (%)	53.1	36.6	10.2
6-Co-ordinate			
Strain energy	193.7	197.3	209.2
Relative H	0.0	3.6	15.5
Expected isomer proportions at 350 K (%)	77.4	22.5	0.1

[a] c: Indicates the isomer with the axial ligand lying on the same side of the co-ordination plane as the majority of the methyl groups. t: Indicates the isomer with the axial ligand on the opposite side to the methyl groups.

This result is consistent with the observation of the *R,S,R,S* and *R,S,R,R* isomers only when the complex is prepared in the absence of other co-ordinating ligands.[1,7] The energy minimized (B) and (C) geometries show significant deviation of the nitrogen donor atoms from the co-ordination plane [up to 0.25 Å for (B)] while for (A), strict planarity is maintained. The deviations in the case of (B) correspond to a tetrahedral distortion with *trans* N–Ni–N bond angles of 166 and 167°. The structure of the trifluoromethanesulphonate salt of four-co-ordinate *R,S,R,S*-$[\mathrm{Ni(TMC)}]^{2+}$ reveals *trans* bond angles of 168°[13] and therefore it appears that the unconstrained model is reasonable.

The results for the equivalent five- and six-co-ordinate complexes are quite different. The (A) isomer is now the most stable in both cases and (C) becomes very much less stable with increasing co-ordination number. These results are consistent with the experimental evidence of Moore *et al.* who found that the presence of strongly co-ordinating solvents resulted in an equilibrium mixture of isomers (A) and (B).[6] Also, the ratio of (A) : (B) of 2 : 1 found in that study is very similar to that predicted by the strain energy minimization calculations.

The strain energy minimization calculations suggest then, that in environments where the four-co-ordinate complex predominates, only isomers (B) and (C) should occur and where additional ligands are present then (A) and (B) should occur with (A) predominating. It has been claimed that the observation of isomer (A) only when $[\mathrm{Ni(TMC)}]^{2+}$ is prepared by *N*-methylation of $[\mathrm{Ni(cyclam)}]^{2+}$ is evidence that (A) is the thermodynamically most stable isomer. However, strongly co-ordinating hydroxy anions were present[2] in that preparation and therefore, isomer (A) would be expected. The relative instability of (B) in acid solution may also be due to co-ordination of counter ions associated with the acid. Thus all the experimental observations listed above can be rationalized in terms of the minimized strain energies.

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