Unexpected and Facile Equilibration of Six-co-ordinate Bis(solvento)-(*R,S,S,R*)(1,4,8,11-tetramethyl-1,4,8,11-tetra-azacyclotetradecane)nickel-(II) Ions with the Five-co-ordinate Mono(solvento)-(*R,S,R,S*)-complexes in Some Co-ordinating Solvents

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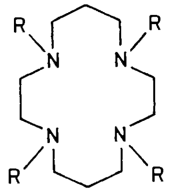
The belief that the complexes of 1,4,8,11-tetramethyl-1,4,8,11-tetra-azacyclotetradecane are thermodynamically stable in the *trans*-III or *R,S,S,R* configuration (A) is shown to be incorrect; there is substantial conversion into the *trans*-I or *R,S,R,S* geometry (B) at a relatively slow rate in some non-aqueous solvents such as dimethyl sulphoxide, but surprisingly rapidly in the presence of a strongly co-ordinating amine such as n-propylamine.

It is well known that two complexes of nickel(II) can be prepared with the quadridentate macrocyclic ligand 1,4,8,11-tetramethyl-1,4,8,11-tetra-azacyclotetradecane (TMC) (**1**; R = Me). Reaction of TMC with $[Ni(H_2O)_6]^{2+}$ in aqueous ethanolic solution produces complex (B) in which the ligand adopts an *R,S,R,S* set of nitrogen configurations. The other structure (A), where the ligand has an *R,S,S,R* geometry, is obtained by *N*-methylation of (*R,S,S,R*)-[Ni(cyclam)]$^{2+}$ [cyclam = (**1**) with R = H].[1] In co-ordinating solvents, or in the presence of unidentate anions, the two isomers (A) and (B) readily form six- and five-co-ordinate adducts, respectively.[1-3]

It is widely believed that the *trans*-III structure (A) is thermodynamically the most stable configuration, and that formation of the relatively 'unstable' *trans*-I complex (B) arises from a low energy kinetic pathway.[1,3] This belief is supported by the apparent inability of the two forms to interconvert, and the observation that in acidic solution (B) undergoes facile hydrolysis to $[Ni(H_2O)_6]^{2+}$ and protonated TMC, whereas (A) is fairly stable in the presence of strong acid. The reaction of cyclam with $[Ni(H_2O)_6]^{2+}$ which gives the *trans*-III geometry (A), is believed to occur by deprotonation of co-ordinated N–H groups which allows rearrangement to the favoured *trans*-III configuration. This deprotonation is not possible for TMC, and so when TMC reacts with $[Ni(H_2O)_6]^{2+}$ the complex is 'trapped' in the 'less stable' structure (B).[3]

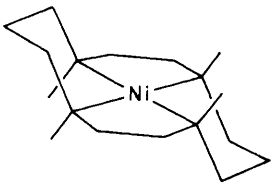
However, whilst investigating both complexes of [Ni(TMC)]$^{2+}$ in a range of donor solvents, we have found that the supposedly stable structure (A) can rearrange to the 'less stable' form (B), and *vice versa*. Equilibration is reached at widely differing rates depending on the solvent used, as shown by some preliminary kinetic data in Table 1. In acetonitrile or aqueous solution the rearrangement is negligible or extremely slow, and this explains why previous studies of these systems failed to reveal the interconversions. In dimethyl sulphoxide or dimethylformamide the reactions take several hours for completion even at elevated temperatures, but in the presence of the strongly co-ordinating ligand n-propylamine in nitromethane solution, it is possible to bring about the rearrangements in a matter of minutes at room temperature.



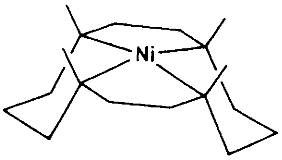
(1)

R = H; cyclam

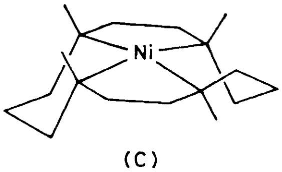
R = Me; TMC



(A)



(B)



(C)

The rearrangements are readily followed either by visible spectrophotometry or by ^1H n.m.r. spectroscopy. In the paramagnetic five- and six-co-ordinate solvento-complexes, the large contact shifts of the resonances in the ^1H n.m.r.

Table 1. Rates of interconversion of (A) into (B) in various co-ordinating solvents.

Solvent	T/K	10^5k/s^{-1}	[B]:[A] at equilibrium
CD_3CN	350	no reaction after 17 h	
D_2O	370	extremely slow	
$DCON(CD_3)_2$	362	*ca.* 10	0.60
$(CD_3)_2SO$	342	1.35[c]	0.33
	353	3.2	0.43
	372[a]	9.6	0.42
Pr^nNH_2[b]	300	*ca.* 10^3	*ca.* 2.0

[a] For the conversion of (B) into (A) in $(CD_3)_2SO$ at 372 K, 10^6k is 6 s^{-1}. [b] n-Propylamine; this reaction was followed by visible spectrophotometry, whereas the other, slower, rearrangements were followed by ^1H n.m.r. spectroscopy. [c] Apparent activation parameters in Me_2SO are $\Delta H^\ddagger$ 62.4 kJ mol^{-1}; $\Delta S^\ddagger$ —156 J K^{-1} mol^{-1}.

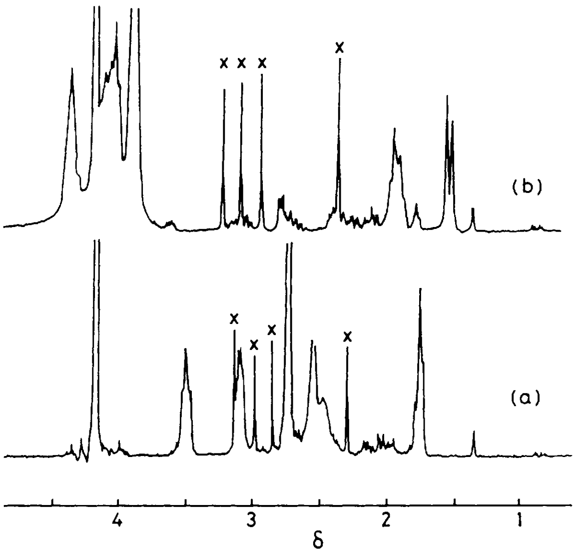


Figure 1. (a) Part of the 400 MHz ^1H n.m.r. spectrum of (B) in [$^2H_3$]nitromethane solution, showing the four sharp N–Me resonances (×) assignable to a small amount of the asymmetric intermediate (C). Spectrum (b) was obtained by adding 1 μl of $(CD_3)_2SO$ to 0.3 cm^3 of the solution used for (a) (see text).

spectra of the non-exchanging macrocyclic ligand are well resolved,[4] and hence the approach to equilibrium is readily monitored in this way. At 372 K, (A) is characterised by resonances in the ^1H n.m.r. spectra at δ − 2.09, 1.92, 5.60, 9.30, 25.60, 28.72, and 61.70, and (B) by resonances at δ −5.89, 6.97, 22.60, 44.50, 47.05, 57.87, and 162.95 [relative to $(CD_3)_2SO$ at δ 2.52]. Integration of the 90 MHz ^1H n.m.r. spectrum in $(CD_3)_2SO$ after 80 h at 372 K reveals an equilibrium ratio of [A]: [B] of *ca.* 2: 1, and the same equilibrium position is reached starting from either pure (A) or pure (B). In the presence of n-propylamine in nitromethane, the supposedly stable form (A) is rapidly converted into (B), and some other minor, and as yet unidentified species. In this reaction the major product is (B) (Table 1).

In the absence of a more detailed kinetic study, one can only hypothesise about the likely mechanism for the rearrangements. Complete dissociation of TMC from Ni^{2+} is not involved since the recombination always produces structure (B). The most plausible mechanism is one in which a single Ni–N bond breaks, to give a terdentate-TMC intermediate, with a donor solvent molecule occupying the vacant co-ordination site at the metal ion, followed by *N*-inversion and chelate-ring-closure to give an (*R*,*S*,*R*,*R*)-intermediate (C). This intermediate would have to undergo one further ring-opening and *N*-inversion to result in the complete rearrangement. Some evidence for the existence of the postulated asymmetric intermediate (C) has been found using 400 MHz ^1H n.m.r. spectroscopy (Figure 1). When the diamagnetic square-planar compound (B) is prepared by reaction of TMC with Ni^{2+}, a minor species is formed with four sharp *N*-methyl resonances at δ 2.30, 2.86, 2.99, and 3.15 (Figure 1). It is possible to solvate (B) preferentially rather than (C) with Me_2SO using a small excess of this solvent in nitromethane [Figure 1(b)]. This causes the overlapping resonances of (B) to shift downfield, thereby revealing more clearly the four sharp *N*-Me resonances, and a number of complex multiplets between δ 1.5 and 3.0, assignable to the asymmetric structure (C). Further evidence that such an intermediate is involved in the rearrangements comes from the observation of different rates for the conversions (A) into (B) and (B) into (A) as shown in Table 1. This observation is inconsistent with a single equilibrium of the type (A) $\rightleftharpoons$ (B), but is explicable if an equilibration of the type (A) $\rightleftharpoons$ (C) $\rightleftharpoons$ (B) occurs.[5]

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