

Structurally Reinforced Cyclen: A Rigidly *trans*-Co-ordinating Twelve-membered Macrocyclic

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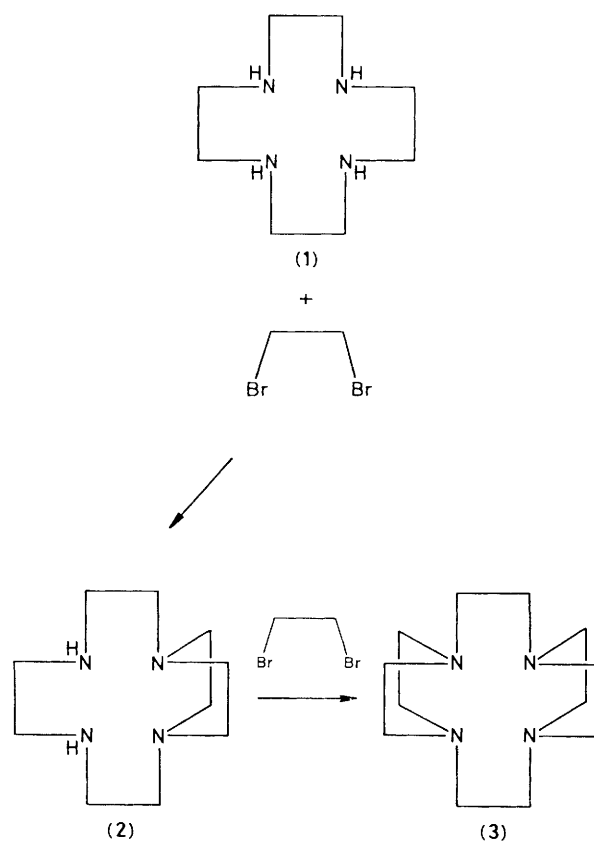
Reaction of 1,4,7,10-tetra-azacyclododecane (cyclen) with 1,2-dibromoethane connects an adjacent pair of secondary amino groups, by means of an ethano bridge, reinforcing the macrocycle and allowing it to circumscribe rigidly nickel(II); an ion to which it would normally be bound in a folded conformation.

The bridging of adjacent secondary amino groups in a macrocyclic ligand provides a convenient method for reducing the propensity of the macrocycle for binding to a metal ion in a *cis*(folded)-conformation rather than the *trans*(planar)-conformation.¹ This is likely to be of particular interest in cases where the modification has forced a macrocyclic ligand to circumscribe a metal ion about which it would rather fold; the resulting combination of a very high ligand field strength and a strained macrocyclic linkage may well produce conditions conducive to unusual reactivity. Such a case, and the subject of this investigation, is the macrocycle 1,4,7,10-tetra-azacyclododecane (hereafter named cyclen) which, whilst it is known in one isolated case,² that of solid state $[\text{Ni}(\text{cyclen})](\text{ClO}_4)_2$, to bind *trans*, will otherwise invariably co-ordinate in the *cis*-fashion^{3,4} and even in this one exception readily folds in co-ordinating solvents to give the *cis*-solvated octahedral derivative as the predominant species in solution.^{2,5}

We have found that cyclen, (1), can readily be bridged by treating it with 1,2-dibromoethane in dry benzene in the presence of solid potassium hydroxide (reflux, 48 h). Small quantities of the dibridged product (3) are formed and can be collected if required, but the major product is mono-bridged-cyclen (2) (irrespective of the ratio of 1,2-dibromoethane to cyclen employed) and since the formation of a single bridge is sufficient to prevent folding (*vide infra*) it is not necessary to collect (3). The mono-bridged cyclen is of volatility intermediate between (1) and (3) and may be separated by fractional sublimation.

Addition of an ethanolic solution of hexa-aquanickel(II) diperchlorate to a solution of (2) in ethanol produces a pale yellow diamagnetic precipitate which analyses as $\text{Ni}(\text{L})(\text{ClO}_4)_2$ [$\text{L} = (2)$]. Dissolution of this compound in water yields a yellow solution which exhibits a single temperature-independent spectral band in the visible region at $24\,900 \pm 100 \text{ cm}^{-1}$ ($\epsilon = 156 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$), typical of square planar nickel(II). There are no other bands in the spectrum which would suggest the presence of equilibrium quantities of the *cis*-diaqua species, as noted with $[\text{Ni}(\text{cyclen})](\text{ClO}_4)_2$,^{2,5} showing that the macrocycle is completely rigid; even the addition of strongly co-ordinating anions such as thiocyanate and azide produced no change in the exclusively square planar spectrum. The addition of cyanide ion does, however, destroy the compound in the usual way.

The energy of the visible absorption band provides a measure of the in-plane ligand field strength⁵ and is remarkable in this case as it exceeds the values reported for $[\text{Ni}(\text{cyclen})](\text{ClO}_4)_2$ [22 575 (ref. 2) and 23 260 cm^{-1} (ref. 5)] by *ca.* 2000 cm^{-1} and appears to be the highest energy yet observed for this particular transition, clearly indicating the effect of reducing the flexibility of an already tightly fitting macrocycle. In contrast, mono-bridging the larger cyclam molecule in the same way¹ actually reduces the energy of this transition from 22 470 to 21 690 cm^{-1} showing that in this example the effect of converting two secondary amino donors into two more weakly co-ordinating tertiary amino groups, a necessary consequence of the bridging process, more than outweighs the perturbation of its rigidity,



Scheme 1

and highlights the significance of this factor in the case of cyclen.

Further evidence for the isomeric purity of *trans*- $\text{Ni}(\text{L})(\text{ClO}_4)_2$ [$\text{L} = (2)$], even when in the presence of a co-ordinating solvent, comes from its ^{13}C n.m.r. spectrum, recorded in $[\text{D}_6]\text{dimethyl sulphoxide}$. This shows the expected five resonances in the region 56.2–50.4 p.p.m. downfield from SiMe_4 . All are of approximately equal intensity and of line width $< 5 \text{ Hz}$. The spectrum is essentially the same as that observed for free (2) except that the resonance due to the carbon atoms in the piperazine ring [observed as a singlet at 49.1 p.p.m. in (2)] appears split into two signals; a consequence of the restrictions upon inversion at the two secondary amino groups which are imposed by co-ordination. It is not possible to deduce from the spectral pattern whether the two N–H groups are in a *cis*- or *trans*-relationship as it would be the same in either case. However, one would strongly suspect that the arrangement is *trans* since it is well known⁶ that in this configuration the proton–proton interactions are minimised. If this is so it follows that the two sides of the piperazine ring must be positioned sym-

metrically above and below the plane of the molecule, since a significant departure from this arrangement would, by destroying the C_2 symmetry, lead to four ^{13}C resonances from the carbon atoms in the piperazine ring rather than the two that are observed.

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