Isomerization and Dealkylation Reactions of Nickel(II) Complexes of Macrocyclic Tertiary Amine Ligands: *X*-Ray Crystal Structures of $\{Ni[1,4,8,11\text{-tetra(2-cyanoethyl)-}1,4,8,11\text{-tetra-azacyclotetradecane}](NCMe)_2\}(ClO_4)_2 \cdot H_2O$ and $\{Ni[1,8\text{-di(2-carbamoylethyl)-}4\text{-(2-cyanoethyl)-}1,4,8,11\text{-tetra-azacyclotetradecane}]\}(ClO_4)_2$

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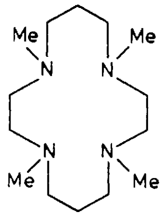
Nitrogen inversion reactions have been observed in nickel(II) complexes of macrocyclic tertiary tetra-amine ligands in which the nitrogen substituents are either 2-cyanoethyl or 2-carbamoylethyl; under certain conditions dealkylative loss of the cyanoethyl substituent occurs but loss of a carbamoyl substituent has not been observed for nickel(II) although it has for copper(II).

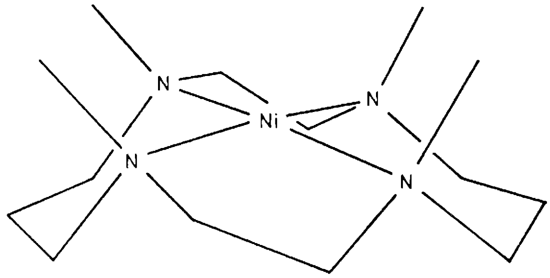
Two isomeric nickel(II) complexes of tetramethylcyclam (TMC) (**1**), having stereochemistries (A) and (B) have been characterized.[1–4] Until recently these isomers were thought to be non-interconvertible. However, Moore and co-workers have recently reported that the two forms can be equilibrated upon heating in donor solvents such as Me_2SO or dimethylformamide and by addition of n-propylamine to their nitromethane solutions.[5] Interconversion occurs extremely slowly in water or acetonitrile even at reflux.

We have observed that Ni^{II} complexes of certain of the functionalized tertiary amine ligands, (**2**)—(**4**),[6–9] undergo isomerization reactions similar to those of $[Ni(TMC)]^{2+}$, even in non-polar media. Dealkylative loss of the functionalized substituent has also been observed in some cases.

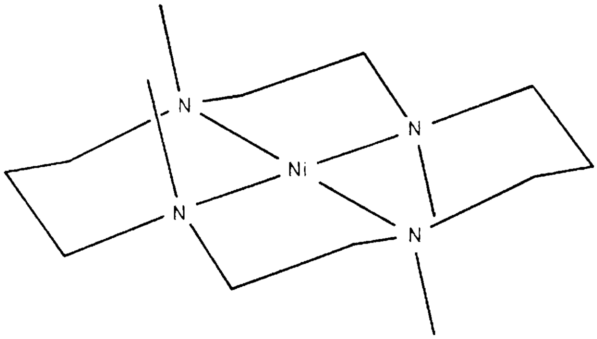
Wainwright reported that the properties of the $Ni(ClO_4)_2$ complex of (**2a**) were consistent with those expected for a complex with stereochemistry (A) but that it underwent hydrolysis on heating in aqueous solution. The hydrolysis



(1)



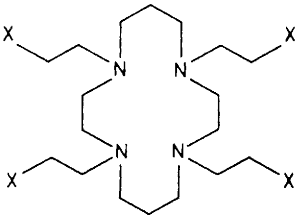
(A)



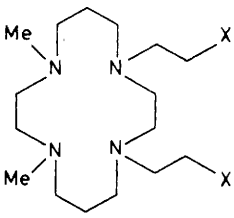
(B)

product was characterized as a complex of (**2b**); however, its properties were not those expected for a complex with stereochemistry (A) and it was suggested that it might have the *trans*-III stereochemistry (B).

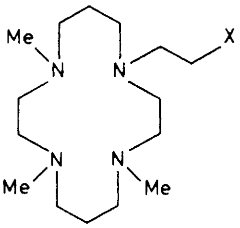
We have prepared this hydrolysis product and have shown, by a single crystal *X*-ray analysis,† that it is actually a complex of the partially hydrolysed, mono-dealkylated, ligand (**5**) but that inversion of stereochemistry has occurred at two nitrogen centres. As the ORTEP drawing given in Figure 1 shows, the nickel ion is six-co-ordinate with the ligand folded such that N(1) and N(3) are co-ordinated axially with N(2) and N(4) and the carbamoyl group oxygen atoms co-ordinated in the equatorial plane. Since N(4) is a secondary amine, its stereochemistry can change *via* the conjugate base; however, the stereochemistry of N(2) presumably cannot change except by dissociation of the nitrogen atom followed by inversion and



(**2a** - **d**)

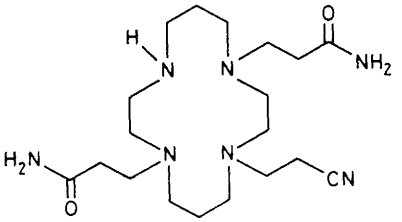


(**3a** - **d**)



(**4a** - **e**)

a, X = CN
b, X = C(O)NH$_2$
c, X = CO$_2$Me
d, X = CH$_2$NH$_2$
e, X = CO$_2$H



(**5**)

rotation about the ring nitrogen–carbon bonds. Our studies on the hydrolysis reaction suggest that it is acrylonitrile that is lost in the dealkylation reaction rather than acrylamide.

The Ni(ClO$_4$)$_2$ complex of (**2a**) isomerizes upon heating in acetonitrile or nitromethane (80% conversion after 16 h reflux in acetonitrile). An *X*-ray structure of the diacetonitrile adduct of the new complex‡ shows that it has stereochemistry (B) (Figure 2).

No evidence for reversibility of the transformation has been obtained; a slower, competitive dealkylation reaction prevents complete conversion to the *trans*-III form. The observed isomerization requires inversion of configuration of two of the nitrogen donors in an intramolecular process. No intermediates were detected by spectrophotometry so that the expected intermediate[5] must not accumulate.

The kinetic product prepared from Ni(ClO$_4$)$_2$ and (**2b**) also isomerizes. The *trans*-III form of the complex (structure

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† *Crystal data:* $C_{19}H_{37}Cl_2N_7NiO_{10}$, orthorhombic, $Pna2_1$, a = 16.454(9), b = 16.730(6), c = 10.338(4) Å, Z = 4, crystals obtained by slow evaporation of an aqueous solution. The structure was solved by heavy-atom techniques and refined using 2254 unique data $[F > 3\sigma(F)]$ measured on a Syntex $P2_1$ diffractometer with Mo-K_α radiation. Hydrogen atom positions were calculated; only their isotropic thermal parameters were refined. Carbon atoms were refined isotropically; all other non-hydrogen atoms anisotropically. Final R value for 259 variables is 0.067.

‡ *Crystal data:* $C_{26}H_{42}Cl_2N_{10}NiO_8\cdot H_2O$, monoclinic, $P2_1/n$, a = 12.726(7), b = 11.712(6), c = 11.182(6) Å, β = 95.40(4)°, Z = 2, crystals obtained by slow addition of acetone to an acetonitrile solution. Data were collected and refined as for the first structure. 2149 unique data gave R 0.070. Although both analytical and i.r. data indicated the presence of a water molecule, its position was not revealed in the final difference Fourier. The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

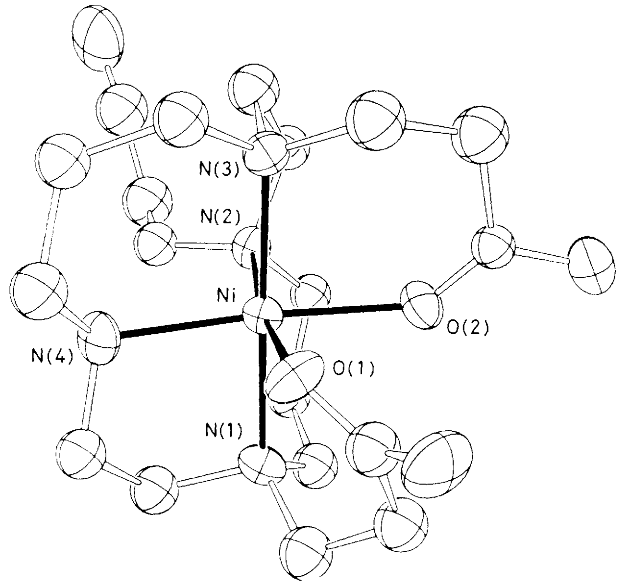

Figure 1. ORTEP drawing of the cation $[Ni(C_{19}H_{37}N_7O_2)]^{2+}$ (30% probability ellipsoids; hydrogen atoms are not shown). Distances (Å): Ni–N(1), 2.121(8); Ni–N(2), 2.174(8); Ni–N(3), 2.130(8); Ni–N(4), 2.106(8); Ni–O(1), 2.079(8); Ni–O(2), 2.081(9). Angles (°): N(1)–Ni–N(3), 177.9(3); O(1)–Ni–N(2), 171.9(3); O(2)–Ni–N(4), 174.9(3).

established by crystallography[10]) was isolated in 92% yield after 2 h reflux in water; longer reaction times did not result in dealkylation. A second form of the complex of (**3b**) was obtained in 48% yield by ion exchange chromatography after 72 h reflux in water. No isomerization of complexes of ligands (**4a**—**e**) has been observed. This leads to the tentative conclusion that at least two appended, ligating groups must be present for isomerization to occur.

Dealkylation of nickel complexes of the carbamoylethyl substituted ligands (**2b**), (**3b**), and (**4b**) has not been observed; however, the Cu^{II} complex of (**4b**) dealkylates upon heating overnight in acetonitrile with sodium methoxide. Facile dealkylation has also been observed for the Cu^{II} complexes of (**4c**) (in acetonitrile with NaOMe) and (**4e**) (in aqueous acid).

Our results indicate that the possibility of both dealkylation and isomerization reactions must be considered in future studies involving tertiary amine ligands that contain β-substituted *N*-alkyl groups. High temperatures and acidic or basic conditions should be avoided in order to maintain the integrity of the kinetic products derived from metal complexation reactions of these ligands. The fact that the Cu^{II} complex of (**4b**) dealkylates whereas the Ni^{II} complex does not, may indicate that such reactions are sensitive to the identity of the metal ion.

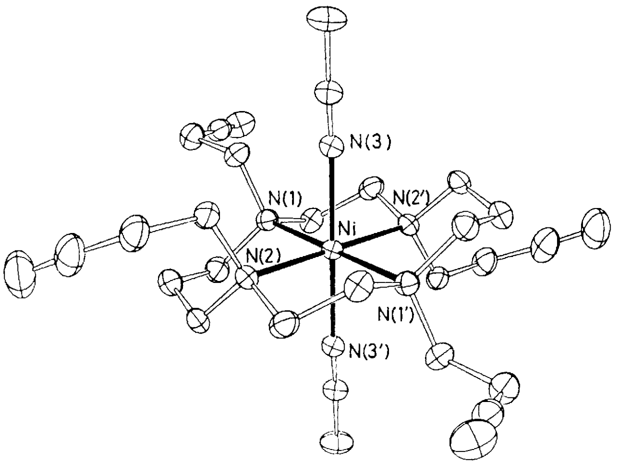

Figure 2. ORTEP drawing of the cation $[Ni(C_{22}H_{38}N_8)(NCMe)_2]^{2+}$ (30% probability ellipsoids; hydrogen atoms are not shown). Distances (Å): Ni–N(1), 2.172(5); Ni–N(2), 2.177(4); Ni–N(3), 2.109(5). Angles (°): N(1)–Ni–N(2), 93.3(2); N(1)–Ni–N(3), 89.9(2); N(2)–Ni–N(3), 88.5(2).

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10 Unpublished results from this laboratory.