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The Crystal Structure of 1,4,8,11-Tetramethyl-1,4,8,11-tetraazacyclotetradecane Nickel(II) Bisperchlorate at 155 K

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Abstract

The crystal structure of the complex 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane nickel(II) bisperchlorate has been determined by an X-ray diffraction study conducted at 155 K. The monoclinic crystals have the space group *Cc* with a = 16.960(5), b = 36.651(8), c = 18.681(5) Å, β = 112.06° and Z = 20. A combination of Patterson and direct methods were used to solve the structure which was refined by a least squares procedure with R = 0.078 and R_w = 0.079, employing 7242 unique reflections with $I \geqslant 2.5\ \sigma(I)$.

The asymmetric unit consists of five independent complex nickel cations and ten independent perchlorate anions. Of the five nickel centres, three are well resolved and of these, two exhibit a marginal tetrahedral distortion of the square planar arrangement of nitrogen atoms around each nickel centre, whilst the third possesses a slight pyramidally distorted square planar character. An average Ni–N bond length of 1.96 Å has been observed. This study unambiguously establishes that for each of these cations, the ligand possesses the R,S,R,S conformation with all four methyl groups on the same side of the NiN_4 plane.

Introduction

It is now well established that the 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane complex of nickel(II) (commonly called nickel tetramethylcyclam or $[Ni(tmc)]^{2+}$) may be prepared as different isomeric forms depending on the synthetic procedure employed. Barefield [1, 2] has reported that direct combination of the tmc ligand with $Ni(H_2O)_6^{2+}$ results in formation of the R,S,R,S isomer (Fig. 1 **A**), whilst methylation of the parent 1,4,8,11-tetraazacyclotetradecane complex, $[Ni(cyclam)]^{2+}$, yields the R,S,S,R species (Fig. 1 **B**).

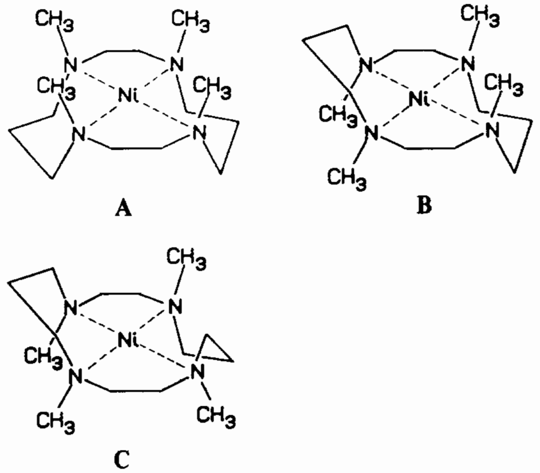

Fig. 1. Stereoisomers of $[Ni(tmc)]^{2+}$. (A) R,S,R,S (B) R,S,S,R (C) R,S,R,R.

Kinetic and equilibrium studies [3–5] involving these complexes have shown that, in solution, both isomers may participate in spin-state equilibria involving diamagnetic four coordinate and paramagnetic five or six coordinate species. The R,S,R,S isomer forms a mono-solvento five coordinate adduct, whereas the R,S,S,R complex adopts an octahedral six coordinate configuration with solvent molecules occupying axial positions. In all of these studies it has been assumed that the product derived from either of the above methods consisted only of a single species of the assigned stereochemical conformation and that no interconversion of isomers occurred. However, more recent evidence has been presented [6, 7] which suggests that under certain conditions, interconversion of isomers may occur and that the synthetic method for the preparation of the R,S,R,S complex does not yield an isomerically pure product.

^{13}C NMR studies conducted by Lincoln [6] on the product formed by combination of tmc with Ni(II), reveal the presence of both R,S,R,S and R,S,R,R isomers (Fig. 1 **C**). However, in nitromethane the asymmetric complex rearranges completely to R,S,R,S. Interconversion of $[Ni(tmc)]^{2+}$ isomers has also been observed by Moore *et al.* [7]. Using ^1H NMR, these workers have shown that interconversion between R,S,R,S and R,S,S,R isomers proceeds in the presence

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of some strongly coordinating solvents to form an equilibrium mixture of the two. The R,S,R,R isomer was proposed as a likely intermediate in the rearrangement process.

Strain energy calculations on the relative stabilities of the three isomers of $[Ni(tmc)]^{2+}$ are consistent with the above findings [8]. Under conditions where the four coordinate complex predominates, only R,S,R,S and R,S,R,R are expected. However, where additional ligands or coordinating solvent molecules are available, a mixture of R,S,R,S and R,S,S,R is favoured, with the latter predominating.

In view of growing interest in the stereochemical aspects of $[Ni(tmc)]^{2+}$ species, it seemed central to these studies to establish the structural nature of the four coordinate state and it is to this end we report the results of an X-ray investigation on the $[Ni(tmc)](ClO_4)_2$ product, previously assigned as R,S,R,S. It was hoped that such a study would resolve any uncertainty as to the stereochemical composition of this complex.

Results

The molecular structure of $[Ni(tmc)](ClO_4)_2$ has been established by an X-ray diffraction study conducted at 155 K. The asymmetric unit consists of five independent complex nickel cations and ten independent perchlorate anions. Of the five nickel centres, three are well characterised and will form the basis of this discussion.

TABLE I. Selected Bond Lengths (Å) for $[Ni(tmc)](ClO_4)_2$

Atoms	n = 1	n = 2	n = 3
Ni(n)–N(n1)	1.935(13)	1.960(14)	1.983(20)
Ni(n)–N(n2)	2.056(13)	1.817(22)	1.974(18)
Ni(n)–N(n3)	1.894(17)	1.996(16)	1.996(14)
Ni(n)–N(n4)	2.001(12)	1.950(13)	1.950(16)
N(n1)–C(n1)	1.593(20)	1.523(33)	1.573(33)
N(n1)–C(n10)	1.405(42)	1.881(27)	1.398(30)
N(n1)–C(n11)	1.631(48)	1.273(28)	1.447(28)
N(n2)–C(n3)	1.414(24)	1.660(30)	1.430(30)
N(n2)–C(n4)	1.297(30)	1.381(43)	1.616(36)
N(n2)–C(n12)	1.686(27)	1.726(50)	1.405(32)
N(n3)–C(n5)	1.661(26)	1.615(38)	1.675(28)
N(n3)–C(n6)	1.556(47)	1.482(32)	1.439(30)
N(n3)–C(n13)	1.483(33)	1.527(32)	1.590(30)
N(n4)–C(n8)	1.492(23)	1.545(31)	1.607(26)
N(n4)–C(n9)	1.575(25)	1.363(29)	1.438(24)
N(n4)–C(n14)	1.295(25)	1.744(25)	1.585(26)
C(n1)–C(n2)	1.602(31)	1.373(32)	1.500(39)
C(n2)–C(n3)	1.376(37)	1.595(36)	1 609(35)
C(n4)–C(n5)	1.529(34)	1.889(45)	1.458(37)
C(n6)–C(n7)	1.261(59)	1.497(35)	1.578(29)
C(n7)–C(n8)	1.773(37)	1.463(37)	1.455(35)
C(n9)–C(n10)	1.225(34)	1.565(32)	1.640(32)

Average bond lengths: Ni–N, 1.960 Å; N–C(methyl), 1.533 Å; N–C(methylene), 1.525 Å; C(methylene)–C(methylene), 1.522 Å.

TABLE II. Selected Bond Angles (°) for $[Ni(tmc)](ClO_4)_2$

Angle	n = 1	n = 2	n = 3
N(n1)–Ni(n)–N(n2)	91.6(6)	99.9(11)	95.2(8)
N(n2)–Ni(n)–N(n3)	86.4(7)	79.4(11)	90.0(8)
N(n3)–Ni(n)–N(n4)	97.9(7)	91.7(7)	93.1(6)
N(n4)–Ni(n)–N(n1)	85.7(6)	88.9(6)	84.3(7)
N(n1)–Ni(n)–N(n3)	170.0(8)	179.1(8)	166.6(8)
N(n2)–Ni(n)–N(n4)	169.4(6)	169.9(11)	168.1(8)
Ni(n)–N(n1)–C(n1)	117.8(10)	111.5(10)	114.9(15)
N(n1)–C(n1)–C(n2)	106.3(15)	121.2(18)	111.7(22)
C(n1)–C(n2)–C(n3)	115.1(20)	107.1(16)	110.2(20)
C(n2)–C(n3)–N(n2)	124.8(19)	106.6(17)	115.0(20)
C(n3)–N(n2)–Ni(n)	116.4(13)	113.7(19)	110.7(15)
Ni(n)–N(n2)–C(n4)	104.1(13)	139.1(18)	102.3(15)
N(n2)–C(n4)–C(n5)	107.7(19)	87.2(21)	111.7(19)
C(n4)–C(n5)–N(n3)	94.9(16)	103.2(19)	108.0(19)
C(n5)–N(n3)–Ni(n)	97.3(11)	109.4(16)	107.3(11)
Ni(n)–N(n3)–C(n6)	109.2(13)	113.9(13)	116.6(14)
N(n3)–C(n6)–C(n7)	123.8(29)	108.1(20)	112.5(17)
C(n6)–C(n7)–C(n8)	100.9(23)	112.9(21)	113.7(17)
C(n7)–C(n8)–N(n4)	109.4(15)	115.9(21)	113.2(18)
C(n8)–N(n4)–Ni(n)	110.5(10)	116.6(13)	118.4(12)
Ni(n)–N(n4)–C(n9)	102.5(9)	118.8(13)	103.2(10)
N(n4)–C(n9)–C(n10)	109 9(20)	102.4(18)	100.6(16)
C(n9)–C(n10)–N(n1)	117.9(37)	101.8(17)	102.8(16)
C(n10)–N(n1)–Ni(n)	100.0(14)	94.6(10)	110.7(14)
Ni(n)–N(n1)–C(n11)	106.3(19)	128.9(17)	109.2(14)
C(n10)–N(n1)–C(n11)	122.4(23)	93.3(14)	98.1(18)
C(n1)–N(n1)–C(n11)	108.5(14)	113.5(16)	113.5(16)
Ni(n)–N(n2)–C(n12)	105.0(10)	100.7(23)	118.7(16)
C(n3)–N(n2)–C(n12)	105.3(15)	102.2(21)	115.2(17)
C(n4)–N(n2)–C(n12)	102.7(17)	85.1(34)	102.8(19)
Ni(n)–N(n3)–C(n13)	111.4(13)	113.4(12)	109.4(13)
C(n6)–N(n3)–C(n13)	110.0(22)	113.3(20)	108.3(15)
C(n5)–N(n3)–C(n13)	115.8(16)	111.0(18)	114.9(15)
Ni(n)–N(n4)–C(n14)	119.1(15)	100.6(9)	111.9(11)
C(n9)–N(n4)–C(n14)	105.3(25)	98.2(20)	113.1(15)
C(n8)–N(n4)–C(n14)	113.1(16)	107.8(14)	102.8(13)

The three macrocyclic centres described here are distinguished by only slight differences in conformation, probably arising from the crystal packing. Selected bond lengths and angles pertaining to this structure are presented in Tables I and II respectively and the atom numbering scheme is shown in Fig. 2. Listings of the final atomic coordinates, calculated and observed structure factors and mean planes equations have been deposited with the Editors.

The arrangement of nitrogen atoms around Ni(1) and Ni(3) is essentially square planar, although some tetrahedral distortion is suggested by the *trans*-N–Ni–N bond angles of 168–170 deg. Mean plane

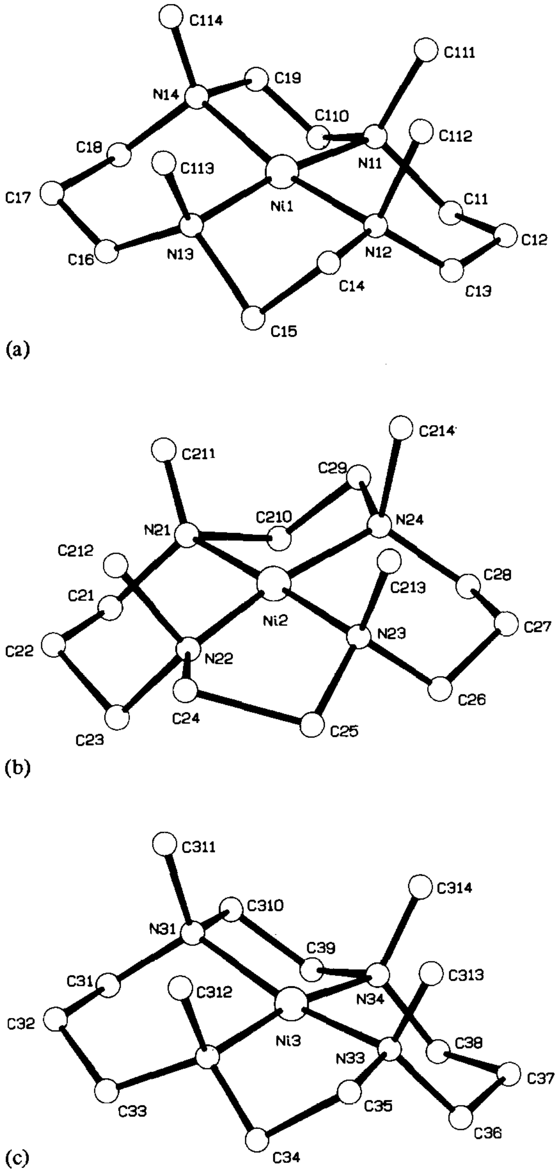

Fig. 2. ORTEP diagrams of: (a) Macrocycle 1, (b) Macrocycle 2, and (c) Macrocycle 3 indicating the atomic numbering scheme and showing the similarities in conformation.

calculations are consistent with this geometry. The two nitrogen atoms *trans* to one another in each macrocycle are located on either side of a least squares plane passing through the nickel atom. Macrocycle 2 possesses a more regular square planar character with *trans*-N–Ni–N angles of 170 and 179 deg. However, unlike the other two nickel environments, the slight distortions are pyramidal in nature. The average Ni–N bond length of 1.96 Å is larger than expected for perfectly square planar complexes [9] but is comparable with such bonds in an environment incorporating deformations of this geometry [10].

This study confirms that for each of the three resolved complex nickel cations, the ligand adopts an R,S,R,S conformation with all four methyl groups on the same side of the nickel–nitrogen plane. The six-membered rings present in each macrocycle assume chair conformations, whilst the carbon–carbon bonds in the two five membered rings adopt the usual skew conformation [11].

A single Ni(3) interaction with a partially occupied oxygen site of a perchlorate anion of 3.0 Å was observed. None of the remaining nickel centres possesses such associations shorter than the sums of the relevant van der Waals radii.

Numerous attempts to interpret the high degree of disorder present in the remaining two macrocycles were unsuccessful and it was therefore not possible to confirm the stereochemistry of these cations. However no evidence to suggest a conformation other than R,S,R,S was obtained.

Experimental

The complex [Ni(tmc)](ClO_4)$_2$ was prepared using the method described by Barefield [1]. Crystals of the product were isolated by slow evaporation of an aqueous solution. Attempts to obtain crystals of the product with anions other than perchlorate were unsuccessful. Due to a high degree of thermal motion and disorder associated with the crystal, intensity data collected at room temperature failed to satisfactorily resolve the ambiguity between possible space groups *C*2/*c* and *Cc* and a further study was therefore conducted at 155(2) K in order to reduce these problems. Structural information reported here is derived from these data.

A density measurement conducted at room temperature indicated the unit cell consisted of 20 formula units and a thorough investigation [12] revealed no simpler unit cell. On the basis of the distribution of chlorine atoms and the disposition of light atoms around two of the nickel centres, the centrosymmetric space group could be discounted and the space group could therefore be assigned as the non-centrosymmetric *Cc*. However, it was noted that substantial regions of the unit cell are near centric and were treated as such during the initial stages of refinement [13]. The coordinates of all nickel and chlorine atoms were determined using a combination of Patterson and direct methods with the remaining non-hydrogen atoms being located from difference maps. Many of the light atoms were disordered; in particular the oxygen atoms in all but two perchlorate ions as well as the ligand atoms of two macrocyclic cations. The relevant sites have been treated in terms of partial occupation by the appropriate atom type.

Refinement was achieved using a least squares procedure minimizing $w\Delta^2$, initially with unit weights and finally the weighting scheme $w = 2.1/(\sigma^2(F) + 0.001F^2)^{-1}$. The refinement converged with values for R and R_w of 0.078 and 0.079 respectively. The final difference map showed peaks of height 1.1 e Å^{-3} or less. It should be noted that because of the large number of parameters involved, a block least squares procedure was required and for this reason, quoted e.s.d. values are very likely to be underestimated.

Anisotropic thermal parameters were applied to all Ni and Cl atoms as well as the light atoms for the three completely resolved macrocycles. Some non-positive definite values were obtained due to the high thermal motion which was evident even at 155 K. The remaining atoms were refined with isotropic temperature factors. The abnormally large temperature factors and e.s.d values obtained in this study reflect the high degree of thermal motion and disorder responsible for the difficulties associated with this structure determination. It is worthy of mention that these and related problems arising from resolution of space group uncertainties, are not uncommon with complexes of this type [14, 15].

Crystal Data

$NiN_4C_{14}H_{32}Cl_2O_8$; M = 514.11, monoclinic, a = 16.960(5), b = 36.651(8), c = 18.681(5) Å, β = 112.06(3)°, V = 11612 Å^3, D_m = 1.53 Mg m^{-3} (293 K), D_c = 1.54 Mg m^{-3}, Z = 20, $F(000)$ = 5400, space group Cc, MoK$\bar{\alpha}$ radiation, ($\lambda = 0.71069$ Å, graphite monochromator), μ = 1.154 mm^{-1}, T = 155(2) K. Intensity data were recorded using an Enraf-Nonius CAD-4 diffractometer and were corrected for Lorentz, polarisation and absorption effects [13, 16] yielding 7242 independent observed reflections [$I \geqslant 2.5\sigma(I)$]; R_{amal} = 0.031. A preliminary photographic study using oscillation and Weissenberg methods was conducted at room temperature.

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