The Crystal Structure of Acetonitrile-1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane Nickel-(II) Bisperchlorate

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Nickel(II) complexes of the macrocyclic ligand 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane (commonly called tetramethylcyclam or tmc) have been of interest for some time. These complexes have demonstrated an ability to participate in spin-state equilibria with solvent molecules such as H_2O and DMF [1, 2]. Two isomeric forms of $[Ni(tmc)]^{2+}$ have been isolated. The R,S,R,S isomer is believed to form a monosolvento five coordinate adduct in solution, whilst the R,S,S,R species adopts an octahedral configuration with solvent molecules in axial positions [1]. More recently, a third isomer R,S,R,R has been proposed in solution using NMR techniques [3], however this species has not been isolated.

We have previously conducted a study of the spin-state equilibrium and solvent exchange kinetics involving R,S,R,S $[Ni(tmc)]^{2+}$ in acetonitrile and have proposed that the complex exists as a mixture of four and five coordinate species in this solvent [4]. Our interest in the change in spin-state of the nickel centre upon solvation has encouraged further investigation of this equilibrium involving X-ray diffraction studies of both the diamagnetic and paramagnetic species isolated from solution in crystalline form. We have recently reported a crystallographic study of the diamagnetic four coordinate R,S,R,S $[Ni(tmc)](ClO_4)_2$ complex [5] and we present here the results of an X-ray diffraction study of $[Ni(tmc)(CH_3CN)](ClO_4)_2$.

Crystals of the title complex were obtained by vapour diffusion of THF into an acetonitrile solution of the $[Ni(tmc)](ClO_4)_2$ complex prepared using the method described by Barefield [6]. These crystals were observed to decompose upon exposure to air and thus the single crystal chosen for the data collection was sealed in a 0.5 Lindeman tube.

Crystal Data

$NiN_5C_{16}H_{35}Cl_2O_8$: $M = 555.17$, tetragonal, $a = b = 9.650(2)$, $c = 13.492(2)$ Å, $V = 1256$ Å^3, $D_m = 1.45$ Mg m^{-3}, $Z = 2$, $D_{calc} = 1.46$ Mg m^{-3}, $F(000) = 584$, Mo Kα radiation ($\lambda = 0.71069$ Å, graphite monochromator), $\mu = 9.93$ mm^{-1}. An Enraf-Nonius CAD-4 diffractometer was used to record in excess of one full hemisphere of reflection intensity data, from which it was apparent that the crystal had Laue symmetry $4/mmm$. Systematic absences unambiguously indicated the space group $P4/nmm$ and the setting possessing the origin at $2/m$ was chosen for this study. The symmetry and space group assignment was confirmed in a separate investigation. Intensity data were corrected for Lorentz, polarisation and absorption effects and of the 5566 measured reflections, 684 were independent ($R_{amal} = 0.021$). Of these, 562 satisfied the criterion $I \geqslant 2.0\sigma(I)$ and were used for subsequent calculations.

Atomic coordinates of the Ni and Cl atoms were deduced from the Patterson synthesis and the positions of the remaining non-hydrogen atoms were determined from subsequent difference Fourier maps. The nickel atom and one of the two chlorine atoms were found to occupy sites of symmetry $4mm$. The other chlorine atom was centred around a site $\bar{4}2m$. This high symmetry is greatly in excess of that expected for the complex cation and the ClO_4^- anions. It was therefore evident that the structure was grossly disordered and that the disorder was of such a nature as to yield the apparent enhancement of symmetry observed around the nickel and chlorine centres. The unexpected symmetry arises from positional disorder of the tmc ligand. Each pair of equatorial nitrogen atoms in the macrocycle is spanned by $-(CH_2)_2-$ and $-(CH_2)_3-$ half weight carbon atom links corresponding to two alternative orientations which contribute equally to the overall structure. These orientations are related by a rotation of 90 deg about the pseudo four-fold axis. Such disorder has previously been observed in similar macrocyclic crystal structures [7]. The disorder in the structure is further complicated by two possible orientations of the staggered methylene carbon links in the five membered rings. These orientations are of equal proportion which accounts for the apparent mirror plane through the metal centre and the midpoints of these bonds. The perchlorate anions are also extensively disordered.

Refinement of the structure was undertaken using the program SHELX-76 [8], treating Ni–N(ring), N–C, C–C (5-membered ring), and C–C (6-membered ring) bond lengths as free variables (d_1, d_2, d_3 and d_4). The methyl groups of the tmc ligand were treated as rigid bodies. This method of refinement has proved successful for other structures involving the tmc ligand [7]. Refinement was achieved using a least-squares procedure minimizing $\omega\Delta^2$. At convergence, the free variables d_1, d_2, d_3 and d_4 had refined to 2.143(6), 1.53(2), 1.49(5) and 1.32(1) Å, respectively with $R = 0.090$ (unit weights). The final difference map showed residual electron density

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between −0.5 and +0.7 e Å^{-3}. Anisotropic thermal parameters were applied to the Ni, N and Cl atoms as well as the carbon atoms of the CH_3CN moiety. Due to the high degree of disorder, carbon atoms of the tmc ligand were refined isotropically.

A perspective view of the $[Ni(tmc)(CH_3CN)]^{2+}$ complex cation is shown in Fig. 1. The geometry about the nickel centre is best described as a distorted square pyramid with the acetonitrile ligand occupying the axial position and the nickel atom displaced from the N_4 plane by 0.34 Å. The Ni–N(ring) bond length of 2.14(1) Å is appreciably larger than the 1.96(1) Å bond length observed in the unsolvated diamagnetic complex [5] and is consistent with a paramagnetic high-spin nickel centre [9].

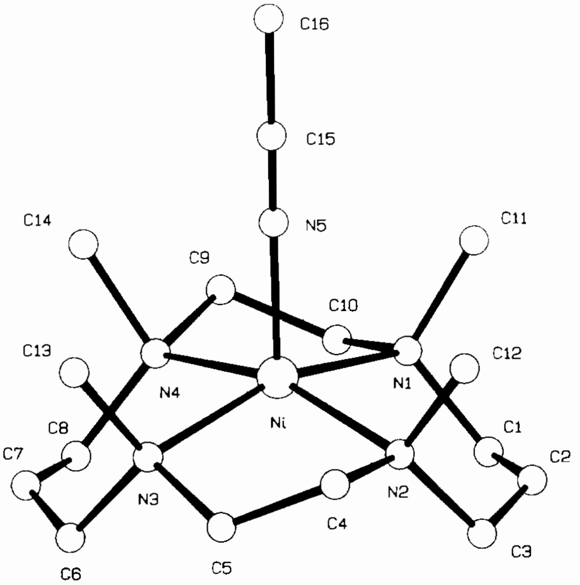

Fig. 1. A perspective view of the $[Ni(tmc)(CH_3CN)]^{2+}$ cation; chelate rings shown correspond to orientation 1 of the tmc ligand generated from the set of disordered carbon atoms. Selected bond lengths (Å) and angles (°): Ni–N(ring) 2.143(6), Ni–N5 1.98(2), N5–C15 1.11(3), C15–C16 1.51(4), N–C(ring) 1.53(2), C4–C5 and C9–C10 1.49(5), C1–C2, C2–C3, C6–C7 and C7–C8 1.32(2). N(ring)–Ni–N5 99.1(3), N5–C15–C16 180(0), all *trans* N(ring)–Ni–N(ring) angles 161.6(4), all *cis* N(ring)–Ni–N(ring) angles 88.5(2).

The stereochemical arrangement of the tmc ligand in both the four and five coordinate complexes is essentially identical. Each of the two six membered rings of the tmc ligand assume chair conformations whilst the two five-membered rings possess the usual skew conformation [10]. This study confirms the R,S,R,S conformation of the ligand with all methyl groups on the same side of the nickel–nitrogen plane. The CH_3CN molecule also coordinates on this side of the plane.

The only other reported structure of this type, with a neutral ligand occupying the fifth coordination site, involves the $[Ni(tmc)(DMF)]^{2+}$ complex cation [2]. Our study of the $[Ni(tmc)(CH_3CN)]^{2+}$ complex cation reveals no major differences in the structural features of these macrocyclic species.

Supplementary Material

Listings of the final atomic coordinates and other data relevant to this structure have been deposited with the Editor-in-Chief.

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