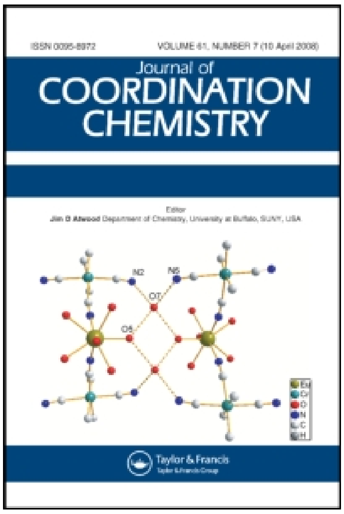

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A Novel Conformation for a Coordinated Macrocycle: The Crystal Structure of $[Ni(12\text{-}aneN_4)(OH_2)_2](ClO_4)_2 \cdot H_2O$; (12-ane$N_4$ = 1,4,7,10-Tetraazacyclododecane)

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A NOVEL CONFORMATION FOR A COORDINATED MACROCYCLE: THE CRYSTAL STRUCTURE OF $[Ni(12\text{-aneN}_4)(OH_2)_2](ClO_4)_2\cdot H_2O$; ($12\text{-aneN}_4$ = 1,4,7,10-TETRAAZACYCLODODECANE)

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The complex $[Ni(12\text{-aneN}_4)(OH_2)_2](ClO_4)_2\cdot H_2O$ (12-aneN_4 = 1,4,7,10-tetraazacyclododecane) has been prepared and its structure determined. The complex crystallizes in the orthorhombic space group $P2_12_12_1$ with $a = 11.173(5)$, $b = 11.976(5)$ and $c = 13.969(4)$ Å. The volume of the unit cell is 1869(1) Å^3. The total reflections collected for $2.0 \leq 2\theta \leq 50.0°$ were 1916 with 1895 being unique and 1659 used in the structure determination. Final values of $R = 0.053$ and $R_w = 0.057$ were obtained. Our results indicate that this six coordinate Ni(II) species has a *cis* or folded geometry and that the coordinated tetraazamacrocyclic ligand exhibits a conformation that is unprecedented in the literature. In this new conformation three of the hydrogens coordinated to the nitrogens point towards the metal centre while only one hydrogen coordinated to a nitrogen points away from the metal centre.

Keywords: Macrocycles, 12-aneN_4, nickel(II), conformation, X-ray structure

INTRODUCTION

There has been an ever increasing interest in the chemistry of tetraazamacrocyclic metal complexes since initial work in the 1960's.[1] These nitrogen-containing macrocyclic complexes exhibit a high degree of kinetic and thermodynamic stability. Additionally, they often have unusual spectral and magnetic properties when compared to non-cyclic analogues. These properties, as well as their redox behaviour, including the ability to stabilize unusual oxidation states of the coordinated metals may be profoundly affected by the macrocyclic cavity size present in these ligands.[1,2] A family of saturated aliphatic macrocyclic amine ligands which have been intensely studied include 12-aneN_4, 13-aneN_4, 14-aneN_4, asym-14-aneN_4, and 15-aneN_4

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(12-aneN_4 = 1,4,7,10-tetraazacyclododecane, 13-aneN_4 = 1,4,7,11-tetraazacyclotridecane, 14-aneN_4 = 1,4,8,11-tetraazacyclotetradecane, asym-14-aneN_4 = 1,4,7,11-tetraazacyclotetradecane, and 15-aneN_4 = 1,4,8,11-tetraazacyclopentadecane).[3] A large body of research has concentrated on the comparison of the properties of various metal complexes of these five ligands. In particular, numerous nickel complexes of these ligands have been synthesized and studied.

Our interest in metal complexes of these tetraazamacrocycles resulted from a communication indicating that the complex $[Ni(14\text{-ane}N_4)]^{2+}$ was an efficient catalyst for the electroreduction of CO_2 to CO.[4] Since that time, we have made efforts towards the incorporation of the nickel 14-aneN_4[5] and 12-aneN_4[6] complexes into a photocatalytic system for the reduction of CO_2 to CO. This work led us to determine the X-ray structure of the complex $[Ni(12\text{-ane}N_4)(OH_2)_2](ClO_4)_2\cdot H_2O$. Our results show that this six coordinate Ni(II) species has a *cis* or folded geometry and the coordinated macrocycle exhibits a conformation that is unprecedented in the literature. In this new conformation three of the hydrogens coordinated to the nitrogens point towards the metal centre while only one hydrogen coordinated to a nitrogen points away from the metal centre.

EXPERIMENTAL

Materials

1,4,7,10-Tetraazacyclododecane was obtained as the hydrochloride salt from Parish Chemicals. Nickel perchlorate was obtained from Fluka Chemicals and used without further purification. Water used in these studies was purified using a Millipore-MilliQ system. All other solvents were of reagent grade and were used without further purification.

Synthesis

The free base ligand, 12-aneN_4, was prepared by dissolving the hydrochloride salt in water and adding base to deprotonate and induce precipitation. The free base was collected by vacuum filtration and used without further purification.

The complex $[Ni(12\text{-ane}N_4)(OH_2)_2](ClO_4)_2\cdot H_2O$ was prepared by the reaction of $Ni(ClO_4)_2\cdot 6(H_2O)$, 2.10 g (5.74 mmol), with 0.23 g (1.34 mmol) of the ligand 12-aneN_4 at room temperature in 70 cm^3 of 95% EtOH. This solution was stirred for 20 min and an equal volume of acetonitrile was added to precipitate the free ligand. The solution was filtered, and the filtrate was reduced to 10% of its original volume by evaporation aided by a stream of nitrogen blowing gently over the solution. This resulted in the precipitation of the nickel 12-aneN_4 complex, while most of the nickel perchlorate remained in solution. The product was collected by vacuum filtration, redissolved in acetonitrile, filtered, and the filtrate again reduced to 10% of the starting volume by nitrogen drying. The precipitated nickel 12-aneN_4 complex was dissolved in ethanol, and the solution was then allowed to evaporate slowly in a hood and the crystals that formed were removed by vacuum filtration. CAUTION: perchlorate salts are known to be EXPLOSIVE under conditions such as mild shock and heat. Care should be exercised when working with these salts.

Crystal Growth and Analysis

X-ray quality crystals of the complex $[Ni(12\text{-ane}N_4)(OH_2)_2](ClO_4)_2\cdot H_2O$ can be obtained by recrystallization from 95% EtOH by simply dissolving the complex in excess ethanol and letting the solution stand in the hood and slowly evaporate to yield large purple crystals.

The crystal structure of this orthorhombic salt, space group $P2_12_12_1$, was determined at room temperature on a Syntex $P2_1$ (upgraded to Nicolet P3 specifications) with a graphite monochromator and MoK_α radiation ($\lambda = 0.71069$ Å). The orientation matrix and lattice parameters were optimized from least-squares refinement to the angular settings of 25 carefully centred reflections with high Bragg angles. Empirical absorption corrections, assuming an ellipsoidally shaped crystal, were employed. The crystal used in the analysis had dimensions $0.30 \times 0.50 \times 0.50$ mm. The total reflections collected were 1916 with 1895 being unique and 1659 used in the structure determination. The SHELXTL 5.1 software package was used for data reduction and refinement.[7] The coordinates of the Ni, Cl, and N atoms were found from direct methods. The positions of the O and C atoms were located from subsequent difference Fourier maps. Several cycles of least-squares refinement of positional and isotropic thermal parameters were performed. Final refinement included variation of all positional parameters and anisotropic thermal parameters on all non-hydrogen atoms. Protons were refined with rigid body constraints and isotropic thermal parameters fixed at approximately 1.2 times the corresponding heavy-atom thermal parameter for the N and C hydrogens. The isotropic thermal parameters for the oxygen protons were fixed at 0.008. Final values of $R = 0.053$ and $R_w = 0.057$ were obtained for all reflections with $F \geq 3\sigma(F)$ and $2.0 \leq 2\theta \leq 50$ degrees. The crystals belong to the orthorhombic space group, $P2_12_12_1$ with $a = 11.173(5)$, $b = 11.976(5)$, $c = 13.969(4)$ Å.

RESULTS AND DISCUSSIONS

The complex $[Ni(12\text{-}aneN_4)(OH_2)_2](ClO_4)_2 \cdot H_2O$ forms X-ray quality crystals upon recrystallization from 95% EtOH. The crystals so isolated are quite large and light purple in colour. These crystals must be cut for X-ray analysis. A summary of crystallographic data is given in Table I.

Hancock and coworkers have classified the conformations observed in the past for macrocyclic tetraaza ligands as TRANS–I, TRANS–II, TRANS–III, TRANS–IV, and CIS–V.[8] Shown in Figure 1 are these established conformations of tetraazamacrocyclic ligands as well as the new conformations we observe for the title complex labelled CIS–VI. In the case of the symmetric ligand 12-aneN_4 the TRANS–IV (+ − − +) conformer is equivalent to the TRANS–III(+ + − −) conformer; thus, the TRANS–IV conformer is omitted for clarity. In the past, only one conformation has been observed for *cis* coordinated macrocycles, CIS–V. In this conformation, two of the hydrogens on the nitrogens lie above the plane of the nitrogens in the macrocycle, and two of the hydrogens lie below this plane. For the CIS–VI conformation only one of the hydrogens on the nitrogens lies below the plane of the nitrogens in the macrocycle, and the other three lie above this plane. Figure 2 shows an ORTEP drawing of the structure of the cation $[Ni(12\text{-}aneN_4)(OH_2)_2]^{2+}$. The ligand is coordinated in a *cis* fashion, with two water molecules occupying the two *cis* coordination sites that remain.

Selected intramolecular bond distances and bond angles are given in Tables II and III, respectively. One of the main characteristics of the coordination geometry for

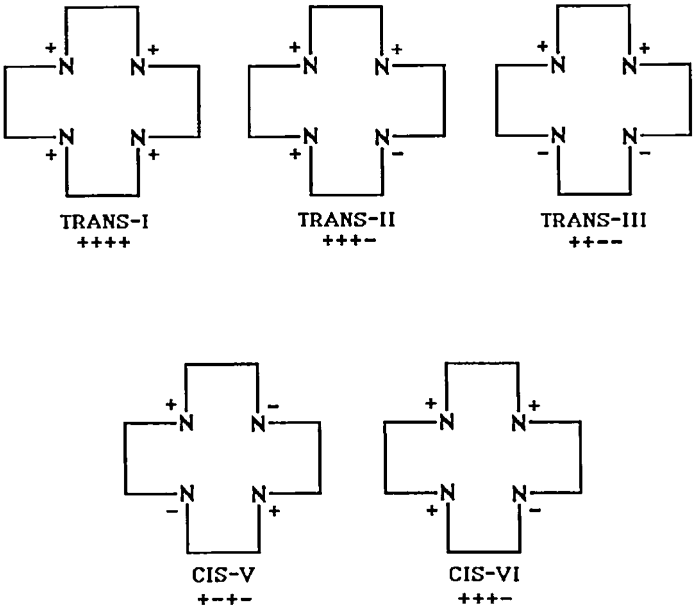

FIGURE 1. Nomenclature for the configuration of coordinated tetraazamacrocycles.[8] The + sign indicates that the hydrogen of the NH group is above the plane of the flattened macrocycle, while the − sign indicates that it is below the plane. For the *cis* conformations, the first + sign refers to a hydrogen on a nitrogen that is *trans* to another nitrogen, indicating that this hydrogen is pointed towards the metal centre, while a − sign would indicate that the hydrogen on a nitrogen is pointing away from the metal centre. The macrocycle shown is 12-aneN_4. For 14-aneN_4 a TRANS-IV conformation (+ − − +) is possible, but this is equivalent to the TRANS-III conformer in the completely symmetric 12-aneN_4 system.

TABLE I
Summary of crystallographic data.

Compound Formula:	$[Ni(12\text{-ane}N_4)(OH_2)_2](ClO_4)_2H_2O$
Diffractometer System:	Syntex $P2_1$
Crystal Class:	Orthorhombic
Space Group:	$P2_12_12_1$ (No. 19)
Lattice Constants:	$a = 11.173(5)$ Å
	$b = 11.976(5)$ Å
	$c = 13.969(4)$ Å
	$V = 1869(1)$ Å^3
Crystal Size:	0.33 × 0.50 × 0.50 mm
Temperature:	Ambient
λ:	0.71069 Å
ρ_{calcd}:	1.51 g cm^{-3}
μ:	13.67 cm^{-1}
Transmission Coefficient:	0.769–0.824
Total Reflections:	1916
Unique Reflections:	1895
Used in Determination:	1659
Final Value of R:	0.053 (0.062 all reflections)
Final Value of R_w:	0.057 (0.068 all reflections)

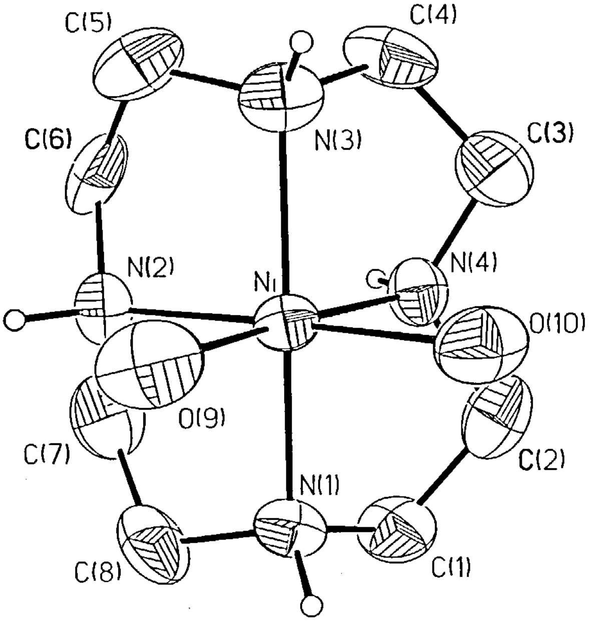

FIGURE 2. ORTEP drawing of the structure of the cation $[Ni(12\text{-}aneN_4)(OH_2)_2]^{2+}$ (where 12-aneN_4 = 1,4,7,10-tetraazacyclododecane).

TABLE II
Selected intramolecular bond distances (Å).

Ni-N(1)	2.103(6)
Ni-N(2)	2.050(6)
Ni-N(3)	2.106(7)
Ni-N(4)	2.070(6)
Ni-O(9)	2.092(6)
Ni-O(10)	2.129(5)

TABLE III
Selected intramolecular bond angles (degrees).

N(1)-Ni-N(2)	84.6(2)
N(1)-Ni-N(3)	158.9(3)
N(2)-Ni-N(3)	84.5(3)
N(1)-Ni-N(4)	82.5(3)
N(2)-Ni-N(4)	98.8(3)
N(3)-Ni-N(4)	81.4(3)
N(1)-Ni-O(9)	97.3(2)
N(2)-Ni-O(9)	86.8(3)
N(3)-Ni-O(9)	100.1(3)
N(4)-Ni-O(9)	174.3(3)
N(1)-Ni-O(10)	96.5(2)
N(2)-Ni-O(10)	172.1(2)
N(3)-Ni-O(10)	96.8(2)
N(4)-Ni-O(10)	89.1(2)
O(9)-Ni-O(10)	85.4(3)

this complex is the amount of distortion necessary to achieve pseudo-octahedral coordination around nickel(II). First, the N(2)–Ni–N(4) angle is 99.1°. This is very distorted from the expected octahedral angle of 90°. Secondly, the angle between N(1)–Ni–N(3) is 159.4°. Again, this is very distorted from the expected 180° for octahedral coordination. However, the bond distances from the nickel metal centre to the ligands vary only by as much as 0.06 Å. Some of the variation seen may be due to strain on the macrocycle (stereoviews of the unit cell, torsional angles, as well as other X-ray data are available as supplementary material from the authors). Hydrogen bonding in this complex is extensive. Several features of the hydrogen bonding are significant. Three of the four protons of the coordinated water molecules are involved in hydrogen bond formation to the oxygen atoms of the perchlorate ions (the fourth hydrogen bonds to the lattice water molecule). The amino protons each form a hydrogen bond to a different perchlorate ion. This is possible in the CIS–VI conformation, but not for the CIS–V arrangement. In the latter, the N(2) and N(4) protons would point to the same region of space, thus restricting the possibilities for hydrogen bonding. The additional stabilization of the crystal structure provided by this extensive hydrogen bonding may be at least partially responsible for the observation of the CIS–VI conformation.

Molecular modelling arguments in the past have not included the CIS–VI isomer as a possible coordination geometry, because the CIS–V case was the only observed *cis* geometry.[8] The addition of the possibility of this CIS–VI geometry may well affect molecular mechanics calculations of the preferred geometry for metal complexes of these tetraaza macrocyclic amines. Certainly, the existence of this conformation *should* be considered and would add more complexity to the problem of theoretical calculations of preferred conformations of this type of macrocyclic ligand.

The existence of *cis* coordination of the 12-aneN_4 macrocycle is of some significance. The coordination behaviour of 12-aneN_4 has frequently been compared to that of larger macrocycles, such as 14-aneN_4, which are known to coordinate in a *trans* fashion. The fact that the 12-aneN_4 macrocycle adopts the highly strained CIS–VI conformation found in this system clearly indicates that the 12-aneN_4 system is too small to girdle the Ni^{2+} ion.

The interesting results of this crystallographic analysis indicate that it may be useful to undertake crystallographic and other types of examinations of a series of pertinent macrocyclic metal complexes. With this in mind, we are currently preparing crystals of a series of nickel macrocyclic complexes of varying ring size, coordinated ligands, and counterions. We hope that the results of this and other studies will lead to a better understanding of the modes of coordination of these ligands in potentially very interesting metal complexes.

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