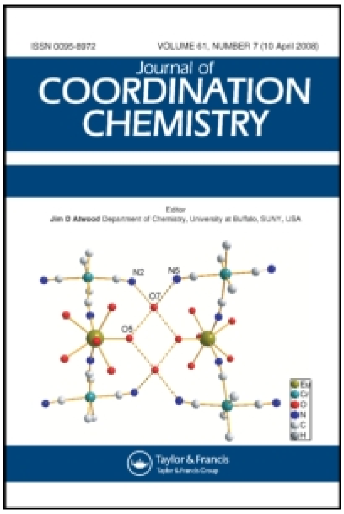

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Unexpected Conformation of the Hydrogen Chloride Salt of [14]aneN_4: An X-ray Structural Examination of [H_2[14]aneN_4H_2]C14 and its Role in Organoaluminum Host-Guest Chemistry

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UNEXPECTED CONFORMATION OF THE HYDROGEN CHLORIDE SALT OF [14]aneN_4: AN X-RAY STRUCTURAL EXAMINATION OF [H_2[14]aneN_4H_2]Cl_4 AND ITS ROLE IN ORGANOALUMINUM HOST–GUEST CHEMISTRY

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The macrocyclic salt [H_2[14]aneN_4H_2]Cl_4 was prepared and its X-ray crystal structure was determined. The salt crystallizes in the orthorhombic space group *Pnna* with unit cell parameters $a = 14.257(11)$, $b = 7.796(5)$, $c = 17.785(9)$ Å, $V = 1976.8(2)$ Å^3, and $D_c = 1.28\ \mathrm{g\,cm^{-3}}$ for $Z = 4$. Least-squares refinement based on 1086 observed reflections ($I > 3\sigma(I)$) converged at $R = 0.055$ ($R_w = 0.075$). The macrocyclic cation is in an unusual exodentate conformation. Additionally, the X-ray crystal structure of the uncomplexed macrocyclic tetradentate secondary amine [14]aneN_4 was determined. The neutral macrocycle crystallizes in the triclinic space group $P\bar{1}$ with unit cell parameters $a = 4.698(3)$, $b = 8.683(5)$, $c = 15.388(12)$ Å, $\alpha = 90.63(6)$, $\beta = 97.38(6)$, $\gamma = 98.99(5)°$, $V = 614.6(8)$ Å^3, and $D_c = 1.08\ \mathrm{g\,cm^{-3}}$ for $Z = 2$. Least-squares refinement based on 1458 observed reflections ($I > 3\sigma(I)$) converged at $R = 0.086$ ($R_w = 0.116$). The endodentate conformation of the neutral macrocycle is stabilized by intramolecular hydrogen bonding by two aza-hydrogen atoms to the remaining two nitrogen atoms. The macrocyclic salt was shown to interact with trimethylaluminum resulting in an organoaluminum host–guest compound capable of accommodating 9.7 toluene molecules per anionic site.

Keywords: Aluminum alkyl, cyclam, macrocycle, X-ray structure, inclusion compounds

INTRODUCTION

The macrocyclic tetradentate secondary amine [14]aneN_4 (1,4,8,11-tetraazacyclotetradecane; commonly referred to as cyclam), initially reported by Van Alphen in 1937,[1] has experienced sporadic popularity over the last fifty years. The advent of oxygen based macrocyclic ligands, crown ethers,[2,3] over the last two decades has served to underscore the significance of this nitrogen based macrocyclic ligand. Particularly significant is the ease with which [14]aneN_4 forms stable complexes with such transition metal ions as Ni(II),[4] Co(III),[5,6] and Rh(III).[6,7] The interest of this laboratory in [14]aneN_4 stems from its potential utility in the preparation of organoaluminum host–guest compounds[8] *via* transition metal ions.

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The conformation of [14]aneN_4 is usually described as endodentate, the four nitrogen atoms residing along the interior of the macrocyclic cavity. Herein, we report the synthesis and first X-ray structural examination of the hydrogen chloride salt of [14]aneN_4, $[H_2[14]aneN_4H_2]Cl_4$. The macrocyclic cation is shown to be in an unusual exodentate conformation. Additionally, the conformation of the salt is compared to the X-ray crystal structure of the neutral uncomplexed [14]aneN_4 macrocycle. Moreover, the role of the macrocyclic amine salt in organoaluminum chemistry is examined with regard to the synthesis of organoaluminum host–guest compounds.

EXPERIMENTAL

General

Standard Schlenk technique[9] was employed in conjunction with an inert atmosphere drybox (Vacuum Atmospheres HE-43 Dri-Lab). Toluene was distilled from sodium/benzophenone under an atmosphere of argon. The nitrogen macrocycle, [14]aneN_4, and trimethylaluminum, both purchased from Aldrich Chemical Co., were used as received. Single crystal X-ray data were collected on a Nicolet R3m/V diffractometer. ^1H NMR data were recorded on a JOEL-FX90 NMR spectrometer.

Synthesis of $[H_2[14]aneN_4H_2]Cl_4$

A reaction vessel was charged with 50 cm^3 of ethanol and [14]aneN_4 (2.50 mmol). An excess of HCl (25 mmol) was subsequently added to the solution. After stirring for 24 h, the solvent was evaporated. The collected solid was dried *in vacuo* and recrystallized from ethanol. The compound was isolated in essentially quantitative yield. ^1H NMR (D_2O): δ 4.64 (m, 4H, N-CH_2-CH_2-CH_2-N), 5.86 (t, 8H, N-CH_2-CH_2-CH_2-N), 6.06 (s, 8H, N(CH_2)$_2$N). Melting point: 210°C (dec.).

Synthesis of $[H_2[14]aneN_4H_2][Al(CH_3)_3)_4Cl_4]\cdot 9.7(C_6H_5)CH_3$

A Schlenk flask was charged with $[H_2[14]aneN_4H_2]Cl_4$ (1.4 mmol) and taken into the drybox where toluene (25 cm^3) and trimethylaluminum (11.7 mmol) were added *via* syringe. Reaction was immediate and quite exothermic. The reaction was judged to be complete within 30 min with the formation of two immiscible liquid layers (the overt indication of the inclusion). ^1H NMR ($(CH_3)_4Si$): δ −0.793 (s, 9H, Al(CH_3)$_3$), 1.62 (s, 3H, (C_6H_5)CH_3), 6.51 (m, 5H, (C_6H_5)CH_3).

Structural Solution and Refinement

X-ray intensity measurements for both [14]aneN_4 and $[H_2[14]aneN_4H_2]Cl_4$ were collected on a Nicolet R3m/V diffractometer using an $\omega/2\theta$-scan technique with MoKα radiation ($\lambda = 0.71073$ Å). The structures of both compounds were solved by direct methods using the SHELXTL[10] package of computer programs. The [14]aneN_4 macrocycle crystallizes in the triclinic space group $P1$ with unit cell parameters $a = 4.698(3)$, $b = 8.683(5)$, $c = 15.388(12)$ Å, $\alpha = 90.63(6)$, $\beta = 97.38(6)$,

$\gamma = 98.99(5)°$, $V = 614.6(8)$ Å^3, and $D_{calc} = 1.08$ g cm^{-3} for $Z = 2$. The asymmetric unit contains two independent half-molecules, each of which is located about an inversion centre. The two molecules are quite similar with no significant differences in bond distances, angles, or conformational angles. Only one of the molecules is described herein. The macrocyclic salt $[H_2[14]aneN_4H_2]Cl_4$ crystallizes in the orthorhombic space group *Pnna* with unit parameters $a = 14.257(11)$, $b = 7.796(5)$, $c = 17.785(9)$ Å, $V = 1976.8(2)$ Å^3, and $D_{calc} = 1.28$ g cm^{-3} for $Z = 4$. The asymmetric unit contains one half-cation situated about an inversion centre in addition to two chloride ions, a water molecule, and an ethanol solvent molecule. The ethanol molecule is disordered about two-fold axes parallel to the *a* and *c* directions. In both compounds, non-hydrogen atoms were refined using anisotropic thermal parameters. Hydrogen atoms were located by standard difference Fourier techniques and were refined using isotropic thermal parameters in both compounds. Least-squares refinement based on 1458 observed reflections ($I > 3\sigma(I)$) for $[14]aneN_4$ converged at $R = 0.086$ ($R_w = 0.116$), while least-squares refinement based on 1086 observed reflections ($I > 3\sigma(I)$) for $[H_2[14]aneN_4H_2]Cl_4$ converged at $R = 0.055$ ($R_w = 0.075$). A summary of crystallographic data for both compounds is given in Table I.

TABLE I
Summary of crystallographic data for $[14]aneN_4$ (I) and $[H_2[14]aneN_4H_2]Cl_4$ (II).

	(I)	(II)
Empirical formula	$C_{10}H_{24}N_4$	$C_{10}H_{28}N_4Cl_4$
Molecular weight	200.38	243.45
Colour; habit	Colourless prisms	
Size	0.60 × 0.40 × 0.30 mm	0.75 × 0.40 × 0.35 mm
Space group	Triclinic, $P\bar{1}$	Orthorhombic, *Pnna*
Unit cell dimensions	*a* 4.698(3) Å	*a* 14.257(11) Å
	b 8.683(5) Å	*b* 7.796(5) Å
	c 15.388(12) Å	*c* 17.785(9) Å
	α 90.63(6)°	
	β 97.38(6)°	
	γ 98.99(5)°	
Volume	614.6(8) Å^3	1976.8(2) Å^3
Molecules/cell	2	4
Density (calc.)	1.08 g cm^{-3}	1.28 g cm^{-3}
Diffractometer	Nicolet R3m/V	
Radiation	Mo-Kα (λ 0.71073 Å)	
Temperature	26°C	
2θ-range	3.00 to 48.0°	3.00 to 45.0°
Reflections collected	2031	1535
Reflections observed	1458	1086
GOF	3.98	1.78
R	0.086	0.055
R_w	0.116	0.075

RESULTS AND DISCUSSION

Reaction of alkali metal or tetraalkylammonium salts with aluminum alkyls was initially reported by Ziegler.[11] When prepared in aromatic solvents these compounds result in organoaluminum host–guest compounds known as liquid clathrates.[8] These novel materials have shown promise in such diverse areas as aromatic separations, coal liquefaction,[8] and optical resolution.[12] To date, only simple tetraalkylammonium salts have been considered in the preparation of these compounds. We, therefore, endeavoured to prepare the hydrogen chloride salt of [14]aneN_4 and utilize it in the synthesis of organoaluminum host–guest compounds. The presence of four anionic sites coupled with the availability of the macrocyclic cavity (for metal ion coordination) are potentially valuable features in organoaluminum host–guest chemistry. In the course of this work we were able to isolate X-ray quality crystals of this salt.

The X-ray crystal structure of the $[H_2[14]aneN_4H_2]^{4+}$ cation is shown in Figure 1. Final atomic coordinates for $[H_2[14]aneN_4H_2]^{4+}$ are given in Table II while selected bond distances and angles are provided in Table III. The macrocyclic cation is situated about a crystallographic centre of symmetry. The four nitrogen atoms are coplanar. The most striking feature of $[H_2[14]aneN_4H_2]^{4+}$, however, is its exodentate configuration (the four nitrogen atoms residing along the macrocyclic perimeter). Associated with each nitrogen atom is a chloride ion. Indeed, the macrocycle has essentially been turned "inside-out". The overall conformation of the macrocycle resembles a "macrocyclic square". Interestingly, only two of the four nitrogen atoms, N(1) and N(1a), are located at the corners of the macrocyclic square. The other two corner positions are occupied by carbon atoms (C(3) and C(3a)). Thus, the remaining two nitrogen atoms, N(2) and N(2a), are components of the hydrocarbon side-chain. While exodentate conformations are quite common for sulfur based macrocycles,[13–16] this is only the second report of a nitrogen based macrocycle assuming such a geometry. The other reported case of an exodentate nitrogen macrocycle was observed for an organoaluminum complex of the tetramethyl derivative of [14]aneN_4, $[Al(CH_3)_3]_4[(CH_3)_4$-[14]ane$N_4]$.[17]

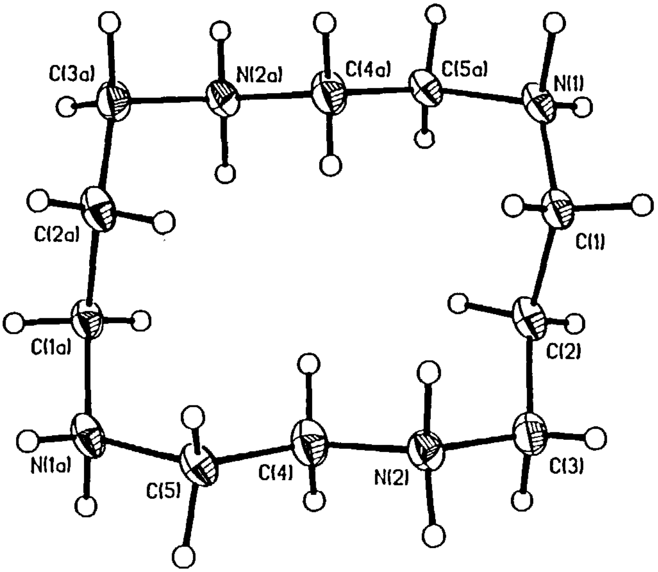

FIGURE 1 A view of the $[H_2[14]aneN_4H_2]^{4+}$ cation showing the atom labelling scheme. Thermal ellipsoids show 35% probability levels.

TABLE II

Atomic coordinates (× 10^4) and equivalent isotropic thermal parameters (Å^2 × 10^3) for $[H_2[14]aneN_4H_2]^{4+}$.

Atom	x/a	y/b	z/c	$U(eq)^*$
N(1)	3647(3)	2010(4)	5662(2)	28(1)
N(2)	4935(2)	4236(5)	3599(2)	27(1)
C(1)	3945(3)	2015(5)	4853(2)	26(1)
C(2)	3532(3)	3508(6)	4416(3)	29(1)
C(3)	3920(3)	3695(6)	3632(2)	31(1)
C(4)	5109(3)	5946(6)	3947(3)	33(1)
C(5)	6131(3)	6425(5)	3881(3)	28(1)
C(6)	2435(12)	771(21)	7129(9)	99(5)
C(7)	2148(12)	1870(24)	7398(12)	120(6)

* Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

TABLE III

Bond distances (Å) and angles (deg) for $[H_2[14]aneN_4H_2]^{4+}$.

N(1)-C(1)	1.499(5)	N(1)-C(5a)	1.501(5)
N(2)-C(3)	1.508(5)	N(2)-C(4)	1.491(5)
C(1)-C(2)	1.518(6)	C(2)-C(3)	1.507(6)
C(4)-C(5)	1.508(6)	C(6)-C(7)	1.063(20)
C(1)-N(1)-C(5a)	117.2(3)	C(4)-N(2)-C(3)	113.2(3)
C(2)-C(1)-N(1)	112.6(3)	C(3)-C(2)-C(1)	113.9(4)
C(2)-C(3)-N(2)	114.5(4)	C(5)-C(4)-N(2)	110.5(4)
C(4)-C(5)-N(1a)	111.3(4)		

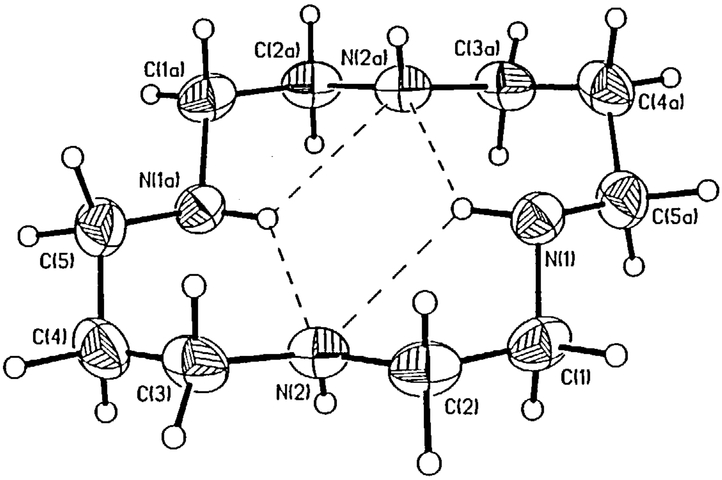

FIGURE 2 A view of the $[14]aneN_4$ molecule showing the atom labelling scheme. Thermal ellipsoids show 35% probability levels.

TABLE IV
Atomic coordinates (× 10^4) and equivalent isotropic thermal parameters (Å^2 × 10^3) for [14]aneN$_4$.

Atom	*x/a*	*y/b*	*z/c*	*U(eq)* *
N(1)	3154(8)	7019(5)	5336(2)	53(1)
N(2)	−2129(9)	6258(5)	4132(3)	52(1)
N(3)	−1699(9)	10772(4)	11108(3)	52(1)
N(4)	2100(9)	8598(4)	10792(2)	51(1)
C(1)	1409(12)	8190(5)	4998(4)	62(2)
C(2)	−99(12)	7706(6)	4093(3)	62(2)
C(3)	−3551(13)	5593(7)	3283(3)	66(2)
C(4)	−5668(13)	4103(7)	3376(4)	70(2)
C(5)	−4251(13)	2758(7)	3734(3)	65(2)
C(6)	336(13)	10280(6)	11807(3)	63(2)
C(7)	814(13)	8626(6)	11613(3)	63(2)
C(8)	2388(13)	7043(6)	10499(3)	59(2)
C(9)	3746(13)	7080(6)	9648(3)	62(2)
C(10)	1880(13)	7576(6)	8850(3)	59(2)

* Equivalent isotropic *U* defined as one third of the trace of the orthogonalized U_{ij} tensor.

TABLE V
Bond distances (Å) and angles (deg) for [14]aneN$_4$.

N(1)–C(1)	1.463(6)	N(2)–C(2)	1.461(6)
N(2)–C(3)	1.459(6)	N(3)–C(6)	1.459(6)
N(4)–C(7)	1.470(6)	N(4)–C(8)	1.451(6)
C(1)–C(2)	1.503(7)	C(3)–C(4)	1.523(8)
C(4)–C(5)	1.508(8)	C(6)–C(7)	1.521(7)
C(8)–C(9)	1.527(7)	C(9)–C(10)	1.522(7)
C(1)–N(1)–C(5a)	113.7(4)	C(3)–N(2)–C(2)	114.8(4)
C(6)–N(3)–C(10a)	113.9(4)	C(8)–N(4)–C(7)	113.5(4)
C(2)–C(1)–N(1)	110.1(4)	C(1)–C(2)–N(2)	109.5(4)
C(4)–C(3)–N(2)	111.8(4)	C(5)–C(4)–C(3)	114.4(5)
C(4)–C(5)–N(1a)	112.4(4)	C(7)–C(6)–N(3)	110.0(4)
C(6)–C(7)–N(4)	108.9(4)	C(9)–C(8)–N(4)	111.3(4)
C(10)–C(9)–C(8)	115.1(4)	C(9)–C(10)–N(3a)	112.0(4)

The exodentate geometry of the [H$_2$[14]aneN$_4$H$_2$]$^{4+}$ cation may best be appreciated by examining the structure of the neutral uncomplexed ligand. The X-ray crystal structure of [14]aneN$_4$ is given in Figure 2. Final atomic coordinates for [14]aneN$_4$ are given in Table II while bond distances and angles are provided in Table V. The difficulty in obtaining X-ray quality crystals of uncomplexed nitrogen based macrocycles is illustrated by the paucity of structural data available on these ligands. This represents, to the best of our knowledge, the first published detailed X-ray structural report on [14]aneN$_4$.[18] As was the case with the macrocyclic cation, the complex resides on a crystallographic centre of symmetry with all four nitrogen atoms coplanar. Particularly noteworthy is the endodentate geometry of the neutral macrocycle. As can be seen from Figure 2, two aza-hydrogen atoms (those bonded to

N(2) and N(2a)) reside along the interior of the macrocyclic cavity. Importantly, each of the two hydrogen atoms is involved in hydrogen bonding with both of the two remaining nitrogen atoms along the cavity. These interactions are indicated as dotted lines in Figure 2. Thus, hydrogen bonding plays a substantial role in maintaining the endodentate geometry of the uncomplexed macrocycle. The two aza-hydrogen atoms not involved in the hydrogen bonding along the interior of the macrocyclic cavity are interacting with neighbouring macrocycles resulting in loosely associated macrocyclic chains. This type of hydrogen bonding is not present in the macrocyclic salt.

The literature reveals only one other structural investigation of a protonated [14]aneN_4 salt. Nave and Truter[19] previously reported the X-ray crystal structure of the diprotonated perchlorate salt of [14]aneN_4. Particularly significant is the fact that this macrocyclic cation remained in the endodentate geometry. While the tetrahydroperchlorate analogue was mentioned as being an intermediate product in the preparative route to the diprotonated perchlorate salt, no attempts at isolation or structural characterization were mentioned. Interestingly, the interaction of HCl with the oxygen-based crown ether 18-crown-6 has recently been reported.[20]

Organoaluminum inclusion compounds known as liquid clathrates have been of interest to us for some time. These inclusion compounds result from reaction of aluminum alkyls with alkali metal or tetraalkyl ammonium ions in aromatic solvents. To date, only simple ammonium salts (*e.g.*, $(C_2H_5)_4NI$) have been examined. The macrocyclic ammonium salt $[H_2[14]aneN_4H_2]Cl_4$ presented an unexplored area of these unusual complexes. Reaction of $[H_2[14]aneN_4H_2]Cl_4$ with trimethylaluminum affords the organoaluminum host compound $[H_2[14]aneN_4H_2][Al_8(CH_3)_{24}Cl_4]$. Upon interaction with toluene two immiscible liquid layers resulted—the overt indication of liquid clathrate formation. The macrocyclic organoaluminum host was shown to interact with 9.7 guest toluene molecules per anionic unit (as determined by ^1H NMR).[8] The macrocyclic cation, being an integral component of the host complex in addition to its vacant cavity, affords another dimension in the organoaluminum host–guest chemistry of liquid clathrates. For example, the cation could transport catalytically important transition metal ions into the inclusion cavity of the host–guest compound.

This study represents a fundamental contribution to organometallic host–guest chemistry and will be used as a benchmark as we further explore the role of macrocyclic amine salts in organoaluminum chemistry.

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SUPPLEMENTARY MATERIAL AVAILABLE

A summary of data collection and refinement (8 pages), tables of crystal data, bond distances and angles, final fractional coordinates, thermal parameters (20 pages), and a listing of observed and calculated structure factors (10 pages) have been deposited with the editor and are available upon request.

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