

Synthesis and Structural Studies of Hydrazino-Crown Ethers and Thermodynamic Studies of Their Interaction with Transition, and Post-Transition Metal Ions and Methyl Ammonium Ion

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Abstract. Hydrazino-crown ethers have been synthesized in only 3 or 4 steps starting from 1,2-diacetylhydrazine. The X-ray crystal structure of protonated hydrazino-19-crown-7 (**2**) showed that one of the hydrazino nitrogen atoms was directed outside the ring cavity. A solvent methanol molecule is held in the cavity of the host ligand by three hydrogen bonds involving two hydrogen atoms bonded to nitrogens of the ligand and the alcohol hydrogen of the methanol. The log *K* values for the interaction of **2** with CH_3NH_3^+ , Ag^+ , Pb^{2+} , and Cd^{2+} were much less than those for the interaction of symmetrical triaza-18-crown-6 (**5**) with the same cations. Hydrazino-crown **2** reduced silver ions to silver metal when a solution of **2** and silver ions in DMSO was allowed to stand for several days.

Key words. Crown ether, hydrazine, X-ray crystal structure, methanol, cation binding, transition metals, post-transition metals.

1. Introduction

In recent years, interest in aza-crown compounds has increased because of their ability to complex a variety of metal and organic cations and anions [1–5]. During the past seven years, about 400 publications concerning the synthesis of aza-crown ethers have been published [6]. The aza-crowns have complexation properties that are intermediate between the all oxygen-containing crowns, which complex strongly with the alkali and alkaline earth metal ions, and the all nitrogen-containing cyclams, which complex strongly with the transition metal cations. The aza-crowns have found application as synthetic receptors in molecular recognition processes. They have anion complexation properties which are similar to those found in certain biological systems [7, 8].

Most aza-crown ethers have ethylene or propylene bridges between the nitrogen atoms. A few aza-crowns have been prepared with one carbon atom between two nitrogen atoms, where the carbon atom is the carbon of a guanidinium, urea, or thiourea moiety [9–13]. These aza-crowns form complexes with cations, anions and amines. Saturated crown ethers containing the hydrazine moiety (no atoms between nitrogen atoms) have been reported only in one short communication [14]. Some

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intermediates for the preparation of small hydrazino-crowns and cyclams, using the Richman–Atkins procedure with tosyl blocking groups on the nitrogen atoms, have been reported [15].

This paper reports the synthesis of one additional hydrazino-crown ether, the crystallographic structure of diprotonated crown **2**, and $\log K$, ΔH , and $T\Delta S$ values for the interaction of three hydrazino- and one triaza-macrocyclic with several cations in two organic solvents.

2. Experimental

2.1. MATERIALS

Nuclear magnetic resonance (NMR) spectra were obtained on a JEOL FX 90Q spectrometer in chloroform- d_3 . Elemental analyses were performed by MHW Laboratories, Phoenix, AZ. All starting materials were purchased from Aldrich Chemical Company. Hydrazino-crowns **2–4** (Figure 1) were prepared as reported in our preliminary communication [14]. Triaza-crown **5** was prepared as reported [16]. 4,5-Dibenzyl-11,15-diethyl-13-methylenyl-1,8-dioxa-4,5,11,15-tetraazacyclohepta-

decane (**1**) was prepared as shown in Scheme 1. Compound **7** was first prepared by reacting 2.2 equivalents of *N*-[2-(2-chloroethoxy)ethyl]acetamide (**A**) with 1,2-dibenzoylhydrazine in DMF at 100–110°C in the presence of sodium carbonate. The reaction mixture was filtered, evaporated and the residue was chromatographed on silica gel using chloroform/ethanol: 30/1 then chloroform/ethanol: 10/1 to give the tetraamide. The tetraamide product was reduced by lithium aluminum hydride in

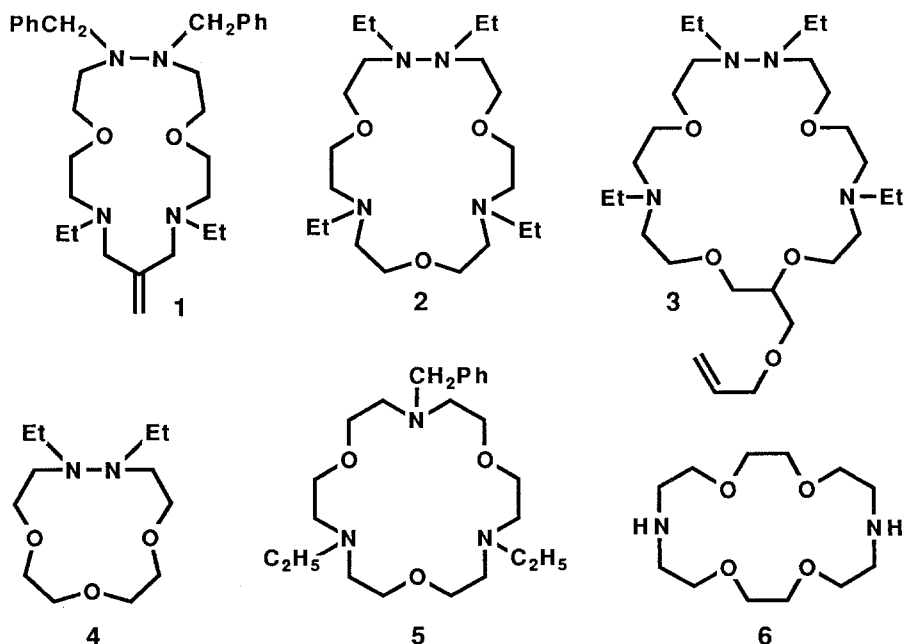
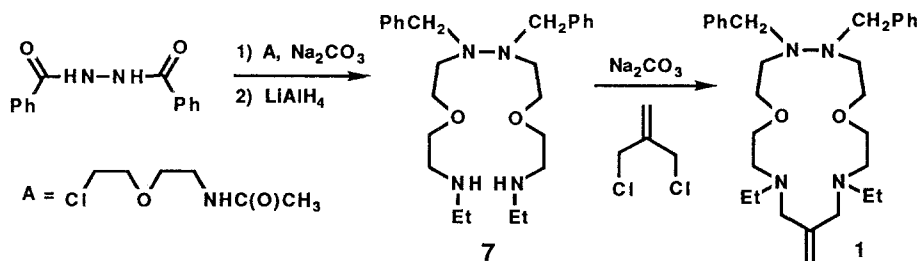


Fig. 1. Macrocyclic compounds



Scheme 1. Preparation of Hydration-Crown 1.

THF at 0–5°C using one equivalent of the hydride per amide group. After the amide was added, the mixture was refluxed for 24 hours, cooled and water, 10% aqueous sodium hydroxide and water were added successively. The resulting mixture was filtered, the residue was washed with THF and the combined THF mixtures were evaporated. The residue was distilled to give a 50% yield of **7** as an oil; b.p. 188–191°C 0.01 mm/Hg. Compound **7** was not further purified but was reacted with 3-chloro-2-(chloromethyl)propene in acetonitrile in the presence of sodium carbonate at reflux temperature. The reaction mixture was filtered, evaporated and the residue was chromatographed on neutral alumina (toluene/ethanol: 100/1) to give a 50% yield of crown **1**; NMR (CDCl₃) δ : 1.0 (t, 6H), 2.6 (m, 12H), 3.2 (s, 4H), 3.5 (m, 12H), 5.1 (s, 2H), 7.2 (m, 10H). Anal. Calcd. for C₃₀H₄₆N₄O₂: C, 72.83; H, 9.37; M⁺, 494.82. Found: C, 72.87; H, 9.30; M⁺ 495.

2.2. DETERMINATION OF THERMODYNAMIC PROPERTIES FOR THE INTERACTION OF 2–5 WITH VARIOUS CATIONS

The log *K*, ΔH , and $T \Delta S$ values for the interaction in methanol and DMSO of **2–6** with CH₃NH₃⁺, Ag⁺, Pb²⁺, Cd²⁺, Cu²⁺, Ni²⁺ and Co²⁺ as determined by calorimetric titration are listed in Table I. Not every cation was reacted with every ligand. The general experimental procedure and calculation methods were reported previously [17, 18].

2.3. X-RAY STRUCTURAL DETERMINATION OF THE PROTONATED FORM OF 2

The crystals of protonated **2** used for the X-ray structure study were prepared by dissolving equimolar quantities of ligand **2** and Pb(ClO₄)₂ in methanol. The solution was kept at 5°C and allowed to evaporate slowly. After ten days, suitable crystals of the compound were removed from the solution and one of the crystals mounted on a Nicolet R3 autodiffractometer which used graphite monochromated Mo *K*_α radiation (0.71073 Å). Chemical analysis along with the density calculations clearly indicated that the compound did not contain lead. The structure analysis showed that the crystal contained a doubly protonated cationic ligand with a charge of 2+; two ClO₄⁻ and a methanol solvent molecule which was located in the cavity of the ligand. Lattice parameters were determined by a least-squares procedure involving angular settings of 20 reflections (5.67° < 2θ < 23.17°). The space group was

Table I. Thermodynamic parameters for the interactions of hydrazino- and aza-crown ethers with various cations.

Compd. No.	Cation	Log <i>K</i>	ΔH (kJ/mole)	<i>T</i> ΔS (kJ/mole)	Solvent (v/v)
2	CH ₃ NH ₃ ⁺	1.52 ^a	-23.7 ± 3.5 ^a	-15.0 ^a	MeOH/H ₂ O (9:1)
2	Ag ⁺	3.46 ± 0.05	-53.9 ± 3.5	-34.1	DMSO
2	Pb ²⁺	<0.5	^b	^b	DMSO
2	Cd ²⁺	<0.5	^b	^b	DMSO
3	CH ₃ NH ₃ ⁺	0.95 ^c	-58.9 ^c	-53.3 ^c	MeOH/H ₂ O (9:1)
4	Cu ²⁺	<0.5	^b	^b	DMSO
4	Ni ²⁺	<0.5	^b	^b	DMSO
4	Co ²⁺	<0.5	^b	^b	DMSO
5	CH ₃ NH ₃ ⁺	4.15 ^a	-33.3 ± 0.3	-9.6	MeOH/H ₂ O (9:1)
5	Pb ²⁺	4.33 ^c	-48.7 ^c	24.0 ^c	DMSO
5	Cd ²⁺	2.62 ^c	-26.4 ^c	-11.4 ^c	DMSO
6	Ag ⁺	6.2 ^d			DMSO
6	Pb ²⁺	4.2 ^d			DMSO

^a Value taken from Reference 14. ^bNo measurable heat was found. ^cOnly one experiment was carried out due to limited amount of material. ^dValue taken from references 24 and 25.

Table II. Crystal and experimental data for diprotonated **2** complex.

Formula	[C ₂₀ H ₄₆ N ₄ O ₃ ·H ₃ OH] ²⁺ [ClO ₄] ₂ ⁻
<i>M_r</i>	621.65
<i>F</i> (000)	1336
crystal size (mm)	0.37 × 0.5 × 0.6
space group	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> (Å)	10.500(4)
<i>b</i> (Å)	8.362(2)
<i>c</i> (Å)	35.877(12)
β (deg)	96.41(3)
<i>V</i> (Å ³)	3130(2)
<i>Z</i>	4
<i>D_x</i> (g cm ⁻³)	1.32
λ (Å)	0.71073
Number of unique reflections collected	4853
Number of reflections used in refinement	3193
Number of unobserved reflections <i>F</i> ≤ 4σ(<i>F</i>)	1660
Final <i>R</i>	0.068
Final <i>R_w</i>	0.087
Goodness of Fit	1.93
average shift/e.s.d.	0.013
largest peaks in Δ map	0.70, -0.42

determined to be *P*2₁/*c* (*h*0*l*, *l* = 2*n* and 0*k*0, *k* = 2*n*). The crystal data and experimental conditions are summarized in Table II. Single crystal data were obtained using a θ -2 θ variable speed scan technique to a $\sin \theta/\lambda$ limit of 0.59. Three reference reflections were measured at 100 reflection intervals to check the crystal

and the electronic stability. A systematic decline in intensity (15% after 5 days) indicated some decomposition of the crystal. The data were corrected for the decrease in intensity and Lorentz and polarization corrections were applied to the data using the data processing program supplied by Nicolet.

The trial structure was obtained using direct methods and the structure was refined using a blocked cascading least-squares procedure. All non-hydrogen atoms were refined anisotropically. The positions of the hydrogen atoms of the methyl group of the solvent molecule were calculated and these atoms were refined isotropically using idealized tetrahedral geometry. Positions for all other hydrogens were obtained from difference maps and their positional and isotropic parameters were refined. The perchlorate containing CL2 was refined anisotropically as an idealized tetrahedral group. The large thermal motion of the oxygens of that ion indicated some disorder which could not be resolved. The structure refined to an R value of 0.068 ($R_w = 0.087$) with weights set equal to $1/\sigma^2(F) + 1.03 \times 10^{-3}F^2$. All computer programs used in the calculations required in the study are contained in SHELXTL [19]. Atomic scattering factors were obtained from the *International Tables for X-Ray Crystallography* [20].

3. Results and Discussion

The new hydrazino-crowns were prepared as shown in Scheme 1 and as reported [14]. *N*-[2-(2-Chloroethoxy)ethyl]acetamide (**A**) is an important intermediate for the preparation of a variety of nitrogen atom-containing crown compounds [16]. 4-Benzyl-10,16-diethyl-1,7,13-trioxa-4,10,16-triazacyclooctadecane (**5**) was prepared in the same manner except benzylamine rather than 1,2-diacetylhydrazine was reacted with **A** in Scheme 1 [16]. The procedures shown in Scheme 1 can be used to prepare hydrazino-crowns with differing numbers of ring nitrogen atoms and with various alkyl groups attached to the various nitrogen atoms [14].

Studies of some open-chain hydrazine compounds have shown that hydrazine ligands possess considerable ability to complex metal and ammonium cations [21]. Crown ethers containing hydrazine moieties built into the ring could have important cation complexation abilities as do the aza-crown compounds [22]. The calorimetric titration studies of the interaction of three of these hydrazino-crowns with various cations show that the introduction of the hydrazine moiety decreases cation binding ability. Log K , ΔH , and $T \Delta S$ values for the 1 : 1 reactions of cations with compounds **2**–**5** are given in Table I. It is seen that the log K values for the interaction of **2**–**4** with all cations studied are considerably lower than those for the interaction of both **5** and **6** with the same cations.

The decreased complexing ability of the hydrazino-crowns was not expected. Since open-chain organic hydrazines form strong complexes with various cations [21], the hydrazine-containing crowns were expected to likewise form strong complexes. The reason for the poor cation complexing ability of macrocycle **2** is probably because of severe steric restraints placed on the two hydrazine nitrogen atoms as shown in the X-ray structure given in the next paragraph. In the case of the diprotonated form of **2**, the structure determination showed that the hydrazine unit twists the macroring so that only one of the nitrogen atoms of the hydrazine unit points into the cavity as shown in Figure 2. The twisted structure also causes

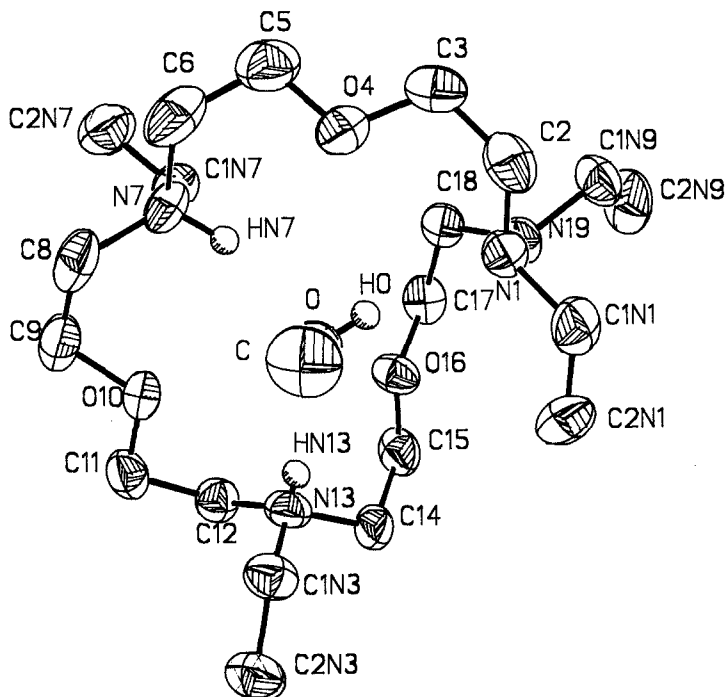


Fig. 2. Perspective drawing of protonated **2** and guest methanol. The ClO_4^- and all hydrogen atoms except those involved in hydrogen bonds are omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level.

the cavity to be smaller and the hydrazine nitrogen atom that is closest to the macrocyclic cavity is hindered from interacting with the metal ions. Thus, a weaker complex would form as the results show.

The solid state structure of protonated **2** and the guest methanol molecule is shown in Figure 2. The atomic parameters are listed in Table III. The solvent molecule is held in the cavity of the cationic ligand by three hydrogen bonds involving HN(7) and HN(13) of the ligand and HO of the methanol molecule. Figure 3 shows the three hydrogen bonds. The hydrogen bond data as well as the interatomic distances between O, the methanol oxygen, and the donor atoms of the ligand not involved in H-bonds are listed in Table IV. These data show that the methanol oxygen atom is nearly equidistant from six of the donor atoms of the host ion. The O-donor atom interatomic distances are about equal to the sum of the van der Waals radii of the atoms (1.4 Å for oxygen and 1.5 Å for nitrogen) and are similar to those found in 18-crown-6 molecules. The nineteenth atom, N(19), a possible donor atom, is excluded from the inside of the cavity (see Figure 3 and Table IV). Unlike most 18-crown-6 complexes, one of the donor atoms, O(16), deviates significantly from the least-squares plane calculated for the other five atoms involved in the coordination of the guest molecule. The deviations of the donor atoms from the least-squares plane calculated for N(1), O(4), N(7), O(10) and N(13) are as follows: N(1), -0.10 Å; O(4), 0.20 Å; N(7), -0.19 Å; O(10), 0.08 Å; N(13), 0.02 Å and

Table III. Atomic positional ($\times 10^4$) and thermal ($\text{\AA}^2 \times 10^3$) parameters of diprotonated 2 complex.

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i>
O	-2037(3)	9781(4)	3889(1)	50(1) ^a
HO	-2076(44)	9202(55)	4061(13)	45(16)
C	-1657(7)	11353(7)	4022(2)	88(3) ^a
N(1)	-2407(4)	8079(4)	4588(1)	44(1) ^a
C(1)N(1)	-3440(6)	8969(7)	4747(2)	60(2) ^a
C(2)N(1)	-4642(6)	9091(7)	4483(2)	80(2) ^a
C(2)	-1214(4)	8199(6)	4845(1)	61(2) ^a
C(3)	-61(5)	7515(6)	4701(2)	60(2) ^a
O(4)	168(3)	8348(4)	4372(1)	58(1) ^a
C(5)	1265(5)	7824(8)	4216(2)	76(2) ^a
C(6)	1400(5)	8756(8)	3874(2)	72(2) ^a
N(7)	284(3)	8621(5)	3569(1)	52(1) ^a
HN(7)	-447(39)	8791(50)	3701(11)	57(13)
C(8)	435(6)	9854(8)	3269(2)	64(2) ^a
C(1)N(7)	101(4)	6929(6)	3419(1)	53(2) ^a
C(2)N(7)	1159(5)	6294(7)	3233(2)	74(2) ^a
C(9)	-537(5)	9745(6)	2937(2)	60(2) ^a
O(10)	-1766(3)	9662(4)	3069(1)	53(1) ^a
C(11)	-2767(5)	9764(6)	2770(1)	53(2) ^a
C(12)	-3941(4)	9037(5)	2917(1)	48(2) ^a
N(13)	-4216(3)	9681(4)	3278(1)	45(1) ^a
HN(13)	-3732(26)	9592(32)	3404(8)	5(7)
C(1)N(13)	-4354(5)	11473(5)	3298(1)	54(2) ^a
C(2)N(13)	-5462(6)	12090(6)	3030(2)	70(2) ^a
C(14)	-5318(4)	8828(6)	3421(1)	52(2) ^a
C(15)	-5009(4)	7109(6)	3510(1)	51(2) ^a
O(16)	-3819(3)	7075(3)	3733(1)	46(1) ^a
C(17)	-3415(5)	5545(5)	3868(1)	50(2) ^a
C(18)	-2368(4)	5796(5)	4180(1)	43(2) ^a
N(19)	-2842(4)	6448(4)	4512(1)	43(1) ^a
C(1)N(19)	-2795(5)	5376(6)	4836(1)	59(2) ^a
C(2)N(19)	-3701(6)	4011(6)	4766(2)	78(2) ^a
CL(1)	2304(1)	9595(1)	2298(1)	50(1) ^a
O(1)CL(1)	1703(4)	11016(4)	2409(1)	84(2) ^a
O(2)CL(1)	2670(4)	8623(5)	2615(1)	91(2) ^a
O(3)CL(1)	3444(5)	10005(5)	2147(1)	108(2) ^a
O(4)CL(1)	1507(5)	8724(5)	2032(2)	122(2) ^a
CL(2)	2624(2)	3234(2)	4029(1)	65(1) ^a
O(1)CL(2)	3197(4)	4641(4)	4098(1)	122(2) ^a
O(2)CL(2)	1377(3)	3380(5)	4062(2)	245(6) ^a
O(3)CL(2)	3135(6)	2153(5)	4274(1)	234(5) ^a
O(4)CL(2)	2777(7)	2767(6)	3682(1)	261(6) ^a

^a Equivalent isotropic *U* defined as one-third of the trace of the orthogonalised *U_{ij}* tensor

Table IV. Hydrogen bond data and other methanol oxygen–ligand donor atom distances in diprotonated **2** complex.

D	H	A	D···A (Å)	H···A (Å)	D—H···A (deg)
N(7)	HN(7)	O	2.971(6)	2.05(4)	163(4)
N(13)	HN(13)	O	2.986(5)	2.35(3)	169(3)
O	HO	N(1)	2.948(5)	2.17(5)	167(5)
O		O(4)	2.986(4)		
O		O(10)	2.989(5)		
O		O(16)	2.949(6)		
O		N(19)	3.728(6)		

O(16), -1.70 Å. The oxygen of the methanol molecule is 0.78 Å above the least-squares plane.

The bond lengths and angles for diprotonated **2** are listed in Table V. They are typical of those found for other crown compounds. Most of the torsion angles have typical low energy values, i.e. approximately 60° about C—C bonds and approximately 180° about C—X (where X = O or N) bonds. However, there are a few notable exceptions. The atypical values are the torsion angles about N(13)—C(14), $65.4(4)^\circ$; C(18)—N(19), $111.8(4)^\circ$ and N(19)—N(1), $-92.7(4)^\circ$. Figure 2 shows these atoms are all below the least-square plane calculated for N(1), O(4), N(7), O(10) and N(13).

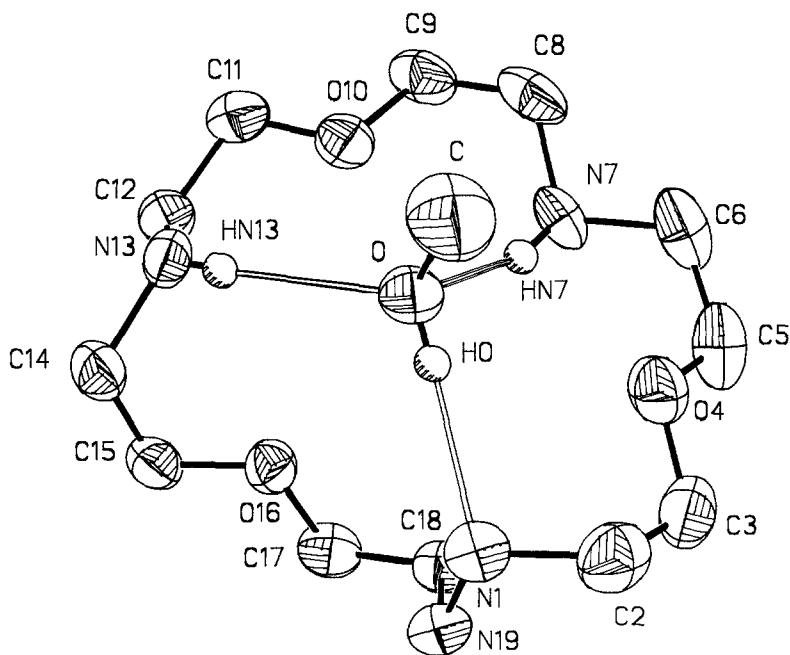


Fig. 3. Perspective drawing of protonated **2** without side chains, showing the three hydrogen bonds which link the methanol to the ligand.

Table V. Bond lengths and bond angles for diprotonated **2**.

1	2	3	1-2 (Å)	1-2-3 (deg)
N(1)	C(2)	C(3)	1.474(6)	115.1(4)
C(2)	C(3)	O(4)	1.484(8)	108.8(4)
C(3)	O(4)	C(5)	1.413(6)	113.8(4)
O(4)	C(5)	C(6)	1.406(7)	109.1(5)
C(5)	C(6)	N(7)	1.472(9)	115.1(4)
C(6)	N(7)	C(8)	1.517(6)	109.2(4)
N(7)	C(8)	C(9)	1.510(8)	114.3(5)
C(8)	C(9)	O(10)	1.484(8)	107.6(5)
C(9)	O(10)	C(11)	1.425(6)	111.6(4)
O(10)	C(11)	C(12)	1.418(5)	105.9(4)
C(11)	C(12)	N(13)	1.520(7)	114.1(4)
C(12)	N(13)	C(14)	1.461(6)	111.4(3)
N(13)	C(14)	C(15)	1.499(6)	111.8(4)
C(14)	C(15)	O(16)	1.501(7)	107.3(4)
C(15)	O(16)	C(17)	1.405(5)	115.2(3)
O(16)	C(17)	C(18)	1.417(5)	107.3(3)
C(17)	C(18)	N(19)	1.495(6)	112.2(4)
C(18)	N(19)	N(1)	1.447(6)	112.3(3)
N(19)	N(1)	C(2)	1.454(5)	114.1(3)

As a result, O(16) is not in the plane as discussed above and the branch of the ring from C(14) to N(19) folds over in such a way as to partially block the back of the cavity and reduce its size.

It is unfortunate that attempts to grow suitable crystals of **2** or its metal ion complexes have been unsuccessful. Without structural studies of these compounds, the cause of the unusual conformational features of diprotonated **2**, particularly the large out-of-plane deviation for O(16) and the resulting reduction in size of the ring, cannot be established. These conformational changes may be caused by the presence of the guest methanol molecule and the hydrogen bonds thus formed or by the presence of the hydrazine group. When attempting to grow crystals of Ag⁺ complexes of **2**, in DMSO, the silver was reduced by the hydrazine group. This is likely a general property of these hydrazine containing compounds. It is well known that hydrazine compounds have been used as reducing agents to produce silver and copper metals from their cations [23].

Added in proof: Other rationale for the decrease in the stability of the hydrazine crowns is found in the dissertation of Geng Wu, BYU, 1989.

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