CRYSTAL STRUCTURE OF 4,7,13,16,21,24-HEXAOXA-1,10-
DIAZONIABICYCLO[8.8.8]HEXACOSANE
SEMIHYDRATE OXONIUM TRIBROMIDE

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The crystal structure of 4,7,13,16,21,24-hexaoxa-1,10-diazeniabicyclo-[8.8.8]hexacosane semihydrate oxonium tribromide, \([\text{H}_2(2.2.2-\text{Crypt})\cdot 0.55\text{H}_2\text{O}]^{2+}\cdot \text{H}_3\text{O}^+\cdot 3\text{Br}^-\) (I) was determined by XRD analysis. The triclinic structure of I (space group \(P\overline{1}\), \(a = 10.026\ \text{Å},\ b = 11.292\ \text{Å},\ c = 13.115\ \text{Å},\ \alpha = 78.37^\circ,\ \beta = 72.11^\circ,\ \gamma = 77.50^\circ,\ Z = 2\) was solved by direct methods; full-matrix least-squares refinement in an anisotropic approximation converged to \(R = 0.055\) for all 4057 independent reflections collected (CAD-4 automatic diffractometer, \(\lambda\text{CuK}_{\alpha}\)).

**Keywords:** X-ray single crystal analysis, 2.2.2-cryptand salts, oxonium salts, bromides.

2.2.2-Cryptand (or 4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane) is a diacidic base capable of forming ionic complexes (salts) with various organic and inorganic acids. The crystal structures of such complexes are of interest for supramolecular chemistry [1], but have received little attention. This communication reports the results of an X-ray diffraction (XRD) analysis of the crystals of a new complex (salt) of similar type: 4,7,13,16,21,24-hexaoxa-1,10-diazeniabicyclo[8.8.8]hexacosane semihydrate oxonium tribromide, \([\text{H}_2(2.2.2-\text{Crypt})\cdot 0.55\text{H}_2\text{O}]^{2+}\cdot \text{H}_3\text{O}^+\cdot 3\text{Br}^-\) (I), where the first component is the 2.2.2-cryptand dication* with a water molecule lying in its cavity and having a site occupancy of 0.55.

Ion complex (salt) I was prepared as follows. An aqueous solution of hydrobromic acid HBr taken in a large mole excess was added dropwise to an ethanol solution of 2.2.2-cryptand, and the resulting mixture was allowed to evaporate at room temperature. In the course of solvent (and excess HBr) evaporation, transparent colorless crystals I settled from the solution. Generally speaking, it was thought that a simpler ion complex (salt) of \([\text{H}_2(2.2.2-\text{Crypt})]^{2+}\cdot 2\text{Br}^-\) type would result; crystals I proved more complex, which was established by further XRD analysis.

The unit cell parameters of the crystal and the three-dimensional set of diffraction intensities for XRD analysis were collected on an Enraf-Nonius CAD-4 automatic diffractometer (CuK_{\alpha} radiation, graphite monochromator). Complex I: triclinic crystals, \([\text{C}_{18}\text{H}_{38}\text{N}_2\text{O}_6\cdot 0.55\text{H}_2\text{O}]^{2+}\cdot \text{H}_3\text{O}^+\cdot 3\text{Br}^-\), \(M = 647.17\); \(a = 10.026(2)\ \text{Å},\ b = 11.292(2)\ \text{Å},\ c = 13.115(2)\ \text{Å},\ \alpha = 78.37(2)^\circ,\ \beta = 72.11(2)^\circ,\ \gamma = 77.50(2)^\circ,\ V = 1364.8(4)\ \text{Å}^3,\ Z = 2,\ d_{\text{calc}} = 1.575\ \text{g/cm}^3,\ \mu(\text{CuK}_{\alpha}) = 58.16\ \text{cm}^{-1},\ \text{space group } P\overline{1}\).

The intensities of 4263 reflections were measured in a hemisphere of reciprocal space \((20 \leq 120^\circ)\) using the \(\omega/20\) scan mode for single crystal I (sized 0.28×0.30×0.75 mm) placed in a thin-walled glass capillary to prevent its decay. For

*Hereinafter the 2.2.2-cryptand dication (with two protonated nodal nitrogen atoms) is called (for brevity) the 2.2.2-dication.

intensity measurements we employed a special mode with the final scan performed for all reflections including very weak ones. After the intensities of 206 pairs of equivalent reflections \(hk0\) and \(hk0\) \((R_{int}=0.036)\) had been averaged, the working set of measured \(F^2(hkl)\) and \(\sigma(F^2)\) was 4057 independent reflections.

The structure of \(I\) was solved by direct methods using the SHLEXS-97 program [2] and refined by the full-matrix least-squares method (on \(F^2\)) using the SHELXL-97 program [2] in the anisotropic approximation of thermal vibrations for all non-hydrogen atoms. The refinement used nearly all data from the working set [including very weak ones with \(l<2\sigma(l)\)], except several reflections showing poor agreement between the experimental and calculated values of \(\omega R\) [2]. In the last cycle of full-matrix refinement, the absolute shifts were less than 0.001 Å.

At different stages of refinement for \(I\), the measured values of \(F^2\) were corrected for empirical absorption using the SHELXA program [2]. Since the exposed crystal was placed in a capillary and had an irregular shape without clear-cut faces, the absorption correction applied by this method was no less correct than the one applied by the other applicable method.

At the first stage of structure refinement for \(I\), the difference Fourier synthesis revealed three rather high peaks \(\Delta\rho\), which corresponded in height to an approximately half-occupied site of the oxygen atom. Two of these peaks, separated by \(\sim 0.85\) Å from each other and lying at the center of the triangle of three independent \(Br^-\) anions, were unambiguously interpreted as \(O\), disordered over two close-lying positions and the \(O'_x\) atom of oxonium \(H_2O^+\). The third peak was found nearly at the center of the 2.2.2-dication void. This peak was also unambiguously interpreted as a half-occupied site \(O_w\) of the oxygen atom of the water molecule. Then for these three sites: \(O_x, O'_x, \) and \(O_w\), least-squares refinement was performed on coordinates, anisotropic thermal parameters, and occupancies.

At the intermediate stage of structure refinement, all \(H\) atoms of the 2.2.2-dication, two \(H\) atoms of the half-occupied water molecule, and three averaged positions of the \(H\) atoms of the disordered \(H_2O^+\) cation were located on the difference Fourier map. Each of the three sites was actually represented by two rather close half-occupied sites of one disordered \(H\) atom.

At subsequent stages of refinement, the coordinates and isotropic thermal parameters of all \(H\) atoms of the 2.2.2-dication were calculated by the least-squares procedure using the riding model [2]. The coordinates of the two half-occupied \(H\) atoms of the water molecule were fixed at the values found from the \(\Delta\rho\) map, and the coordinates of six nearly half-occupied sites \(H_{1x}, H_{2x}, H_{3x}\), and \(H'_{1x}, H'_{2x}, H'_{3x}\) of three \(H\) atoms of the disordered \(H_2O^+\) cation were fixed at the values calculated geometrically from the coordinates of the averaged positions found in the difference Fourier synthesis (see above).

For exposed crystal \(I\), the isotropic extinction coefficient \(g=0.0010(2)\) was also refined by least-squares analysis [2]. In the last cycle of full-matrix refinement, the absolute shifts were less than 0.001σ for all 292 varied parameters of structure \(I\). The final coordinates and thermal parameters of atoms are listed in Table 1 (with site occupancies of the disordered atoms indicated in the Note to Table 1).

The final \(R\) indices are \(R=0.049\) and \(wR_2=0.135\) for 3500 observed reflections with \(l\geq2\sigma(l)\); \(R=0.055\) and \(wR_2=0.150\) for all 4057 independent reflections collected; the goodness-of-fit \(S=1.02\) (for determination of \(wR_2\) and \(S\), see [2]). In the final difference Fourier synthesis, \(-0.38<\Delta\rho<0.45\) eÅ\(^{-3}\). The \(f\) curves used and the anomalous dispersion corrections to them (\(\Delta\rho''\) and \(\Delta\rho''''\)) are taken from [3].

Figure 1 shows a fragment of the molecular ion packing in the crystal structure of \(I\). The bond lengths and the bond and torsion angles are given in Table 2.

The 2.2.2-dication in \(I\) has the following mean bond lengths of covalent bonds: \(N^--C\) 1.503(5) Å, \(O--C\) 1.422(5) Å, and \(C--C\) 1.501(6) Å. The mean length of \(N^--C\) bonds in the dication is almost the same as the corresponding mean statistical bond length, the mean length of \(O--C\) bonds is slightly smaller, and that of \(C--C\) bond is much smaller: \(N^+(sp^3)--C(sp^3)=1.502(15)\) Å for \(HN^--(C)\) fragments, \(O--C(sp^3)=1.426(11)\) Å for \(C(sp^3)--O--CH_2--C(sp^3)\) fragments, and \(C(sp^3)--C(sp^3)=1.524(14)\) Å for \(C(sp^3)--CH_2--CH_2--C(sp^3)\) fragments [4]. The stated effective shortening of the transannular \(C--C\) bonds is typical of \(O--CH_2--CH_2--O\) fragments and is well-known for crown ethers [5].