The need for nonlinear optical materials has led us to investigate in a concentrated acidic medium HX (X = Cl, Br, F and I) the chemical interaction between organic molecules, such as diamine and triamine and bismuth(III) oxide, which contain active lone pairs. In the particular case of ethylenediamine, we previously described the chemical preparation and the crystal structures of NH3(CH2)2NH3[BiI4]2·4H2O1 and [NH3(CH2)2NH3]BiCl5·2H2O.2 In these compounds the bismuth atom shows a tendency towards distorted octahedral coordination with some rather long Bi–X bonds, which is attributed to an aspherical distribution of lone-pair electrons at Bi(III). These compounds are interesting groups of crystals because they show a phase-transition ferro-paraelectric related to the motion of organic cations.3 Our investigations were extended to five aliphatic diamines, NH2(CH2)nNH2 (with n = 2 to 6), in order to examine the effect of the flexible cation on the geometry of the bismuthate(III) halogenide polyhedra. The title compound is the first salt obtained during investigations of the quaternary system Bi2O3–NH2(CH2)2NH2–HBr–H2O. In the present work, we describe the chemical preparation and the crystal structure of bis ethylenediammonium bromide hexabromobismuthate(III) monohydrate.

The complex crystals were obtained by dissolving in a concentrated HBr (48%) solution a stoichiometric mixture of NH2(CH2)2NH2 and Bi2O3 (molar ratio 4/1). The resulting aqueous solution was then kept at room temperature. After several weeks of evaporation, pseudohexagonal prism-shaped monocrystals of bis ethylenediammonium bromide hexabromobismuthate(III) monohydrate appeared in the solution. Chemical analyses of bismuth atoms and bromide anions were carried out. A thermogravimetric analysis showed that the complex crystallized with one water molecule per formula unit. Experimental conditions used for the single-crystal data collection are reported in Table 1. The positional parameters for the bismuth atoms were obtained from a three-dimensional Patterson map, while the remaining atoms were found from successive difference Fourier maps. After introducing anisotropic thermal factors for the nonhydrogen atoms and isotropic ones for H atoms, the hydrogen atoms were localized and optimized to fixed positions. Their contributions were isotropically introduced into the calculation, but not refined. Corrections were applied for Lorentz and polarization effects and for absorption. The final anisotropic full-matrix least-squares refinement resulted in convergence of the R factor to 0.0392 (Rw = 0.0664) incorporating the weighting scheme.

Table 1 Crystal and experimental data

<table>
<thead>
<tr>
<th>Formula: [NH3(CH2)2NH3]2BrBiBr6·H2O</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formula weight: 910.61</td>
</tr>
<tr>
<td>Crystal system: monoclinic</td>
</tr>
<tr>
<td>Space group: P21/a</td>
</tr>
<tr>
<td>a = 11.960(6)Å</td>
</tr>
<tr>
<td>b = 13.993(2)Å</td>
</tr>
<tr>
<td>c = 12.272(6)Å</td>
</tr>
<tr>
<td>β = 92.10(2)˚</td>
</tr>
<tr>
<td>Z = 4</td>
</tr>
<tr>
<td>V = 2052.42(1)Å</td>
</tr>
<tr>
<td>Dm = 2.947</td>
</tr>
<tr>
<td>T = 298 K</td>
</tr>
<tr>
<td>Crystal size: 0.56 × 0.89 × 0.1</td>
</tr>
<tr>
<td>Goodness of fit: 0.917</td>
</tr>
<tr>
<td>No. of unique data measured: 5967</td>
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<tr>
<td>No. of reflections used: 3131</td>
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<tr>
<td>No. of parameters: 155</td>
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<tr>
<td>2θ max = 59.98 with Mo Kα</td>
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<tr>
<td>Absorption correction: numerical</td>
</tr>
<tr>
<td>R = 0.0392</td>
</tr>
<tr>
<td>(Δρ)max = 1.393 e/Å³</td>
</tr>
<tr>
<td>(Δρ)min = -1.649 e/Å³</td>
</tr>
<tr>
<td>Measurement: Enraf-Nonius CAD4</td>
</tr>
<tr>
<td>Program system: ShelXL 97</td>
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<td>Refinement: full matrix</td>
</tr>
</tbody>
</table>

CCDC 650084
\[ w = 1/[\alpha(F_{o}^{2}) + (0.0347P)^{2} + 0.0000P^{2}], \]
where \( P = \text{Max}(F_{o}^{2}, 0) + 2F_{e}^{2}/3). \)

The atomic arrangement of the complex is depicted in Fig. 2. The structure of the title compound consists of the \( \text{[NH}_{3}\text{(CH}_{2}\text{)_{2}}\text{NH}_{3}]^{2+} \) cation, isolated \( \text{[BiBr}_{6}]^{3-} \) anions octahedral, \( \text{Br}^{-} \) anions, and water molecules. Each Bi atom is surrounded by six Br atoms forming a distorted octahedral configuration with Bi–Br bond lengths ranging from 2.8137(8) Å to 2.8863(8) Å. These values are comparable to those reported to date.\(^1\,^2\) The bond angles within the \( \text{[BiBr}_{6}]^{3-} \) anion of the complex, listed in Table 3, do not indicate any stereochemical activity of the Bi lone electron pair, which, however, has not been observed in other halogenobismuthates(III) either.

\[ \text{[BiBr}_{6}]^{3-} \text{octahedra are connected to the isolated bromide anions (Br\text{^{-}})} \text{ by relatively weak O(W) –H · Br hydrogen bonds, so that anionic clusters of composition [BiBr}_{7}(\text{H}_{2}\text{O})^{4-} are formed in the structure.} \]

\[ \text{The organic groups, present as dications, [NH}_{3}\text{(CH}_{2}\text{)_{2}}\text{NH}_{3}]^{2+}, have a trans configuration with a non crystallographic inversion center. Table 3 reports on the principal geometrical features of the [NH}_{3}\text{(CH}_{2}\text{)_{2}}\text{NH}_{3}]^{2+} groups.}\]

References