

Introduction

Studying the literature one may conclude that the tendency of HgX₃⁻ to polymerize in the solid state of A:Hg′X salts is much less pronounced than in the corresponding Cd salts. Halogenomercurate anions (HgX₃)⁶⁺, (HgX₄)²⁻, (HgX₅)⁻ and (HgX₆)⁴⁻ are often reported. The structure of AHgX₃ depends on the respective cations and halogens. As the cation becomes larger and the electronegativity of the halogen smaller, the polymerization tendencies of HgX₃⁻ are found. Another tendency is the coordination of the halogen atoms such as bridging, hydrogen bonding halogen ‐ Y, etc., information on phase transitions and on the lattice dynamics becomes available. The ⁸¹Br NQR and ¹²⁷I NQR on the bond distances (halogen ‐ M) of halogen complexes and coordination or a trigonal bipyramidal coordination is sometimes found in the bromine complexes. Recently Köffer et al. [4] found that in orthorhombic (CH₃NH₃)HgBr₃ completely planar HgBr₃³⁻ ions exist and two extra Hg ‐ Br contacts complete a trigonal bipyramidal coordination around Hg.

Halogen NQR spectroscopy offers a wealth of information on the solid state properties of halogeno complexes. Besides the high sensitivity of halogen NQR on the bond distances (halogen ‐ M), the coordination of the halogen atoms such as bridging, hydrogen bonds halogen ‐ Y, etc., information on phase transitions and on the lattice dynamics becomes available. The ⁸¹Br and ¹²⁷I NQR spectrum of Hg atom. The Cl atom tends to like a linear two-coordination. NH₄HgCl₃ [3] contains distorted HgCl₆ groups polymerized into layers in which axial Hg ‐ Cl bonds are shorter than equatorial ones. On the other hand, in the Iodine complexes a tetrahedral coordination is mostly found. Possibly the coordination in the bromine complexes may be intermediate between the chlorides and the iodides. Three coordination or a trigonal bipyramidal coordination is sometimes found in the bromine complexes. Recently Köffer et al. [4] found that in orthorhombic (CH₃NH₃)HgBr₃ completely planar HgBr₃³⁻ ions exist and two extra Hg ‐ Br contacts complete a trigonal bipyramidal coordination around Hg.

8¹Br NQR and Crystal Structure of Ethylammonium Tribromomercurate(II), CH₃CH₂NH₃HgBr₃

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The ⁸¹Br NQR triplet spectrum of (CH₃CH₂NH₃)²⁺(HgBr₃)⁻ was measured in the range 77 K to near the m.p. (99–106°C). v₁ decreases strongly with increasing temperature, exhibiting 136.784 MHz at 77 K and 128.129 MHz at 298 K. v₂ decreases from 82.060 MHz at 77 K to 76.322 MHz at 298 K. v₃ increases with temperature, showing v₃ = 81.292 MHz at 77 K and 84.903 MHz at 298 K. Replacement of the ammonium hydrogens by deuterium produces a negative shift of v₁ and positive ones of v₂ and v₃ at high temperatures. These shifts change with temperature from [−0,1] up to [~200] kHz. The crystal structure of the title compound was determined at room temperature: P 2₁/m, Z = 2, a = 1021.6(8) pm, b = 643.0(6) pm, c = 691.8(6) pm, β = 96.96(4)°. The coordination of the mercury atom by the bromines is trigonal bipyramidal; by formation of bridges Hg ‐ Br ‐ Br and Hg by one of the three bromines (Br²⁻) of the planar HgBr₃³⁻ ions a double chain of trigonal bipyramids is formed, running along the b-axis of the crystal. Br⁴⁻ and Br²⁻ are single bonded to Hg. The hydrogen bonds N ‐ H ‐ Br and N ‐ H ‐ Br(²) (twice), connect the Hg ‐ Br chains to planes lying parallel to the bc plane at x = 0. The relations between the Br-NQR spectrum and the structure are discussed.

Key words: Mercury(II) Bromide Complex, Crystal Structure, ⁸¹Br NQR, ¹⁴N ‐ ²D isotope effect, H-bonding.

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Experimental

The title compound was prepared from a dilute hydrobromic acid solution (or a methanol-acetone solution) containing stoichiometric amounts of HgBr₂ and CH₃CH₂NH₃Br. CH₃CH₂NH₃Br was obtained by adding hydrobromic acid to an aqueous CH₃CH₂NH₂ solution. C, H, and N analysis was consistent with the chemical formula; found/calc.; weight %: C: 4.98/4.94; H: 1.66/1.66; N: 2.67/2.88. The partially deuterated compound (CH₃CH₂ND₃)₂HgBr₃ was prepared by mixing CH₃CH₂ND₃Br and HgBr₂ in a dilute D₂O solution of DBr where CH₃CH₂ND₃Br was prepared from repeated cycles of dissolution of CH₃CH₂NH₃Br (CH₃CH₂ND₃Br) in D₂O and successive evaporation of D₂O. The preparation of the D compounds were done under an atmosphere of N₂ in a glove bag. For the X-ray diffraction experiments, small single crystals were selected.

The ⁸¹Br NQR spectra were registered by cw methods (super-regenerative NQR spectrometer). The signals were recorded on a recorder through a lock-in amplifier with Zeeman modulation. The temperature was measured by a Cu-constantan thermocouple with an estimated accuracy within ±1 K.

The crystal structure was determined by single crystal methods with a 4-circle diffractometer. From the collected diffraction intensities, after appropriate correction of absorption and Lorentz-polarization factor, the structure was determined by the direct method [9] and refined by a least squares method [10]. Due to the heavy atoms Hg and Br we could not locate some of the hydrogen atoms. However, symmetry considerations are helpful in locating the hydrogen positions. The experimental conditions for the structure determination are given in Table 1.

Results

Ethylammonium tribromomercurate crystallizes in monoclinic space group C₂h-P2₁/m, with Z = 2 formula units in the unit cell. The lattice constants are a = 1021.6(8) pm, b = 643.0(6) pm, c = 691.8(6) pm, β = 96.96(4)°. In Table 1 some crystallographic data are. In Table 2 we have listed the atomic coordinates and the thermal parameters. Table 3 contains intramolecular distances and angles and the geometry of the hydrogen bond scheme. In Fig. 1 we show the projection of the unit cell along the c direction onto the ab plane. The characteristic features of the structure can be recognized. Double chains of trigonal

Table 1. Experimental conditions for the crystal structure determination and crystallographic data of (CH₃CH₂NH₃)₂(HgBr₃)². Diffractometer: Stoe-Stadi 4; wavelength: 71.069 pm (MoKα). Monochromator: Graphite (002); Scan ø/2θ. M = 486.3.

<table>
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<th>Crystal habit</th>
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<tr>
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</tr>
<tr>
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<tr>
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<tr>
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</tr>
<tr>
<td>F(000)</td>
<td>R(F) = 0.058</td>
</tr>
<tr>
<td>Rₐ(F)</td>
<td>0.053</td>
</tr>
<tr>
<td>Rₘ(F)</td>
<td>0.057</td>
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<tr>
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<tr>
<td>c/pm</td>
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<tr>
<td>β/°</td>
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</tr>
<tr>
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<tr>
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<tr>
<td>qobs/mg·m⁻³</td>
<td>3.58(1)</td>
</tr>
<tr>
<td>Point positions</td>
<td>Atoms Hg, Br⁽¹⁾, Br⁽²⁾, Br⁽³⁾, C⁽¹⁾, C⁽²⁾, N, H⁽c₂⁻¹⁾, H⁽n₁⁻¹⁾, in 2(e) x, 1/4, z; x, 3/4, z; H⁽c₁⁺⁾, H⁽c₂⁺⁾, H⁽n₁⁺⁾ in 4f, x, y, z, x = 1/2 + y, z, x, 1/2 - y, z.</td>
</tr>
</tbody>
</table>
Table 2. Positional and thermal parameters of the atoms in the unit cell of \((\text{CH}_3\text{CH}_2\text{NH}_3)^+\) \((\text{HgBr}_3)^3\). The temperature factor is of the form \(T = \exp(-2\pi^2(\frac{h^2a^2}{a^2} + \frac{k^2b^2}{b^2} + \frac{l^2c^2}{c^2} + \frac{2hlka}{a} + \frac{2hlb}{b} + \frac{2lck}{c}))\). Some of the positions of the hydrogen atoms were calculated, see text. Because of the special position of all atoms in \(y\), \(U_{13}\) and \(U_{23}\) are set zero.

Table 3. Intra- and interatomic distances and angles in the structure of \((\text{CH}_3\text{CH}_2\text{NH}_3)^+\) \((\text{HgBr}_3)^3\). The distances \(d\) are given in pm and the angles in degree. Some of the distances and angles \(C-H, N-H, C(1)-N-H, C(1)-C(2)\) are calculated on the basis of the symmetry, ideal tetrahedral angle, and \(d(C-H) = d(N-H) = 108\) pm, see text.

Fig. 1. Projection of the unit cell of \((\text{CH}_3\text{CH}_2\text{NH}_3)^+\) \((\text{HgBr}_3)^3\) along \(c\) onto the \(ab\) plane. The hydrogen bonds \(N-H \cdots Br\) are marked by dashed lines. It is seen by looking at Fig. 2, which shows the projection of the unit cell along \(\{010\}\) onto the \(ac\) plane.

We have not been able to find the hydrogen atoms in the difference Fourier synthesis. However, the symmetry of the space group is here of great help. All heavy atoms (Hg, Br, N, C) are located on the \(ac\) plane at \(y = 1/4\) (Figure 1). Assuming ideal tetrahedral coordination at the atom \(C(2)\) it follows that the hydrogen atoms of the \(C(1)-H\) group must lie symmetrically to this plane at the point position 4(f) of the space group. Assuming the angle \(H-C(1)-H\) to be 109° and the distance \(d(H-C) = 108\) pm, we find the coordinates of the hydrogen atoms \(H(1)\), \(H(2)\), \(H(3)\), and \(H(4)\) given in Table 3. With the same argument we have determined...
the positions of the hydrogen atoms of the group C(2)H3. We fix the atom H(C2,1) at the point position 2(e) with constraint for d(C–H) and \(\angle(H–C–H)\). The same arguments and the same procedure is applied to the NH3 group for H(N,1) in 2(e), and H(N,2) and H(N,3) in 4(0).

The 81Br NQR spectrum is a triplet with some unusual features. The frequencies \(v_i\) of both protonated and deuterated salts are plotted as a function of \(T\) in Figure 3. At \(T=77\) K \(v_1\) is by a factor of 1.7 higher than \(v_3\) in frequency. At 77 K \(v_2\) and \(v_3\) differ little. However the temperature coefficient \(dv/\) \(dT\) is positive for \(v_3\), opposite to those of \(v_1\) and \(v_2\). In Table 4 frequencies at selected temperatures are reported. By deuteration all lines are affected in their frequency up to \(\sim 200\) kHz. The sign of the shifts of \(v_2\) and \(v_3\) is opposite to that of \(v_1\).

Discussion

\((\text{CH}_3\text{CH}_2\text{NH}_3)^\oplus(\text{HgBr}_3)^\ominus\) is an ionic salt. For the discussion we adopt the atomic (ionic, van der Waals) radii \(r(\text{NH}_3\ominus)=163\) pm, \(r(\text{Br}^\ominus)=196\) pm, and within distances of N–H \(\cdots\) Br we have to discuss hydrogen bonds N–H \(\cdots\) Br. \(r_{vdw}(\text{Br})=185\) pm, \(r_{vdw}(\text{CH}_3,\text{CH}_3)=170\) pm [11]. With the rather large limits of error, there is nothing unusual as much as the geometry of the ethylammonium ion is concerned. The distances C–C and C–N are in the range one finds for aliphatic ammonium salts.
In Fig. 4 we show the full unit cell in an overall view. Further, in Figure 5 the trigonal bipyramidal configuration around Hg atom as the unit of the double chain is depicted. The double chain, which the HgBr$_3^+$ ions form by polymerization via Hg–Br–Hg bridge bonds, is running along [010]. Clearly seen are the hydrogen bonds N–H⋯Br which connect the cations in the bc plane. The symmetry of the structure leads to a planar HgBr$_3^+$ ion with two nearly equal distances Hg–Br of 258 pm, $d$(Hg–Br$^{(2)}$) and $d$(Hg–Br$^{(3)}$) and a shorter distance $d$(Hg–Br$^{(1)}$)= 245 pm. The angles Br–Hg–Br are grouped around 120° with deviations of ±15°, see Table 3. Two atoms Br$^{(2)}$ of neighboring HgBr$_3^+$ ions are coordinated with each HgBr$_3^+$, and in this way a trigonal bipyramid is the subunit of the double chains. In Fig. 5 this unit is shown, and the angles and distances within the trigonal bipyramid are given in Table 3.

The distances $d$(N⋯Br)$\leq$ 360 pm point toward hydrogen bonds N–H⋯Br. As Table 3 shows, there are three contacts N⋯Br which are considerably shorter than 360 pm, namely $d$(N⋯Br$^{(2)}$): 344 pm and two $d$(N⋯Br$^{(3)}$): 347 pm. $d$(N⋯Br$^{(1)}$) is quite long (419 pm) and we can not expect a hydrogen bond N–H⋯Br$^{(1)}$.

In Table 3 we have listed the distances and angles of the hydrogen bond network. Br$^{(2)}$ is connected with the cation by one hydrogen bond, and Br$^{(3)}$ accepts two hydrogen bonds N–H⋯Br, from symmetry considerations of equal length. Due to the hydrogen bonds, we have a lattice of planes parallel to the bc plane and centered at $x=0$, which are formed by the HgBr$_3$ double chains and the cations. These planes are hold together by van der Waals forces. Br atoms and CH$_3$ groups interact at the plane (1/2,0,0).

The present structure is compared with that of (CH$_3$NH$_3$)$_2^{+}$(HgBr$_3$)$_{\theta}$ [4] in which the pyramidal configuration around the Hg atom of planar (HgBr$_3$)$_{\theta}$ and the double chain are found too. Due to a small size and higher symmetry of (CH$_3$NH$_3$)$_2^{+}$, the (CH$_3$NH$_3$)$_2^{+}$ salt has a more compact and higher-symmetry structure (Cmcm) at room temperature. All heavy atoms lie on the ab plane and the C–N and Hg–Br$_{briding}$ bonds are along the b axis such that two terminal Br atoms are equivalent. The bond distances Hg–Br$_{terminal}$ = 252.7, Hg–Br$_{briding}$ = 256.5 in
(HgBr$_3$)$_2$, and Hg $\cdots$ Br bridging $= 319.2$ pm as an intermolecular bond are compared to the corresponding values in Table 3. The H-bonds N-H $\cdots$ Br are expected only for the terminal Br atoms with $d$(N $\cdots$ Br) of 348 pm in the $ab$ plane and of 367 pm (though a little long) between the successive layers of $ab$, so that whole double chains are connected by H-bonds in the (CH$_3$NH$_3$)$_2$ salt.

In the $^{81}$Br NQR spectrum, $v_1$ is much higher than $v_2$ and $v_3$. From the theory of nuclear quadrupole interaction (the simplest is the frequency dependence on the bond distance $d$(Hg-Br) should be $v=a \cdot 1/d$(Hg-Br)$^3$. Therefore, it is correct if we assign $v_1$ to Br$_{1}^{(1)}$ because $d$(Hg-Br$_{1}^{(1)}$) is the shortest (245 pm) of the three distances within the planar configuration HgBr$_3$. The distance is a little shorter than the 248 pm (with other four short contacts of 323 pm) of $d$(Hg-Br) in HgBr$_2$ [12]. Coincident with this, the $^{81}$Br NQR frequencies in HgBr$_2$ [13] are 130.933 and 129.907 MHz at 77 K, which is lower than $v_1$. Furthermore, Br$_{1}^{(1)}$ is neither affected by a hydrogen bond nor is it involved in a bridging configuration Hg-Br-Hg. Also the temperature dependence of $v_1$ is as one expects from the Bayer theory [14]. $v_3$ increases with increasing temperature. Therefore $\varphi_{z}$ of the electric field gradient tensor increases with increasing temperature. We assume, that the intermolecular bonds such as the hydrogen bonds weaken with temperature because of the activation of thermal motions of the molecules. Br$_{2}^{(2)}$ is incorporated into one H-bond and a Hg-Br-Hg bridging bond, while Br$_{3}^{(3)}$ is incorporated into two equivalent H-bonds. It seems that H-bonds are more feasible compared to the Hg-Br-Hg bond because the cation may undergo larger motions in the present type crystals. This leads to the assignment $v_3 \leftrightarrow$ Br$_{3}^{(3)}$ and consequently the assignment $v_2 \leftrightarrow$ Br$_{3}^{(3)}$. The observation [5] that $dv/dT$ of bridging Br atoms in the (CH$_3$NH$_3$)$_2$ salt is also negative seems to support the above assignment. Further, the signal intensity of $v_2$ is weaker than $v_3$ (Table 4). The bridging Br atom in the (CH$_3$NH$_3$)$_2$ salt shows also a weaker intensity than the terminal Br atom (which is incorporated into the H-bonds scheme). The assignment $v_1 \leftrightarrow$ Br$_{3}^{(3)}$ is done by qualitative arguments and is tentative. For a final decision single crystal Zeeman split NQR experiments have to be done.

Going from the (CH$_3$NH$_3$)$_2$ salt to the (CH$_3$CH$_2$NH$_3$)$_2$HgBr$_3$ the frequencies range of the $^{81}$Br NQR spectrum is widened by ca. a factor three: For the (CH$_3$NH$_3$)$_2$ salt the frequencies spread in the range 111 to 91 MHz at 77 K and 101 to 87 MHz at 298 K. However, the mean values of the frequency coincide well in both salts: 100 MHz at 77 K and 97 MHz at 298 K. This may show that the different schemes of H-bonding and Br $\cdots$ Hg intermolecular bonding in the two compounds change the negative charges on the respective Br atoms of (HgBr$_3$)$_2$, so that their total net charges remain constant.

Frequency lowering in $v_2$ and $v_3$ (and resultant raising in $v_1$) from the mean values may mostly be ascribed to the H-bonding and Hg $\cdots$ Br intermolecular bonding. We inquired the direction of the intermolecular bond with respect to the main Hg-Br bond on which the effect on the frequency may depend. Hg $\cdots$ Br$_{2}^{(2)}$-Hg is 96.3°. For H-bonds we obtain: $H$$(N_2)^{\cdot}$ $\cdots$ Br$_{2}^{(2)}$-Hg = 94.1°, $H$$(N_2)^{\cdot}$ $\cdots$ Br$_{3}^{(3)}$-Hg = 102.5°. All values are close to 90° though there are large uncertainties on the positions of H atoms. This may show that the electron populations of $p_x$ or $p_y$ may be effectively reduced by these intermolecular bonds, which may result in the large decrease of resonance frequencies [6].

$v(T)$ curves show no evidence of phase transition in the (CH$_3$CH$_2$NH$_3$)$_2$ salt from 77 K up to near the m.p. (99~106°C). The successive phase transitions observed in the (CH$_3$NH$_3$)$_2$ salt [5] are tentatively ascribed exclusively to the motion of the (CH$_3$NH$_3$)$_2$ ion having a more symmetrical shape compared to the ethyl ammonium ion.

The frequency shifts produced by deuteration are similar to those observed in (CH$_3$NH$_3$)$_2$HgBr$_4$ [6], showing a small difference. From qualitative considerations [6] we expect frequency shifts by deuteration on the Br atoms incorporated into H-bonds. If H $\cdots$ Br-Hg $\sim$ 90°, then we expect positive shifts at high temperatures and negative shifts at a low temperature limit. If H $\cdots$ Br-Hg $\sim$ 180°, the reverse shifts may be expected. With H$(N_2)^{\cdot}$ $\cdots$ Br$_{2}^{(2)}$-Hg = 102.5°, the shifts of $v_3$ seem to coincide with the above prediction. The shifts are positive at high temperatures and become almost zero around 77 K. With H$(N_2)^{\cdot}$ $\cdots$ Br$_{2}^{(2)}$-Hg = 94.1°, the shifts of $v_3$ are also positive at high temperatures, but in contradiction to the above prediction their values tend to increase with decreasing temperature. Further, for $v_1$, whose Br atoms seem not to be concerned in the H-bonding scheme, we find negative shifts which become larger with increasing temperature. For an understanding of these deviations from the above prediction we may need an addi-
tional explanation in which cationic motions possibly take part. It may also be helpful to investigate the isotope-effects in a series of alkylammonium halogeno-mercurates and to classify the types of effects.