^{81}Br NQR and Crystal Structure of Ethylammonium Tribromomercurate (II), $CH_3CH_2NH_3HgBr_3$ *

Hiromitsu Terao, Tsutomu Okuda [1], Kichiro Koto, Shi-qi Dou [2], and Alarich Weiss [2]

Faculty of Integrated Arts and Sciences, Tokushima University, Minamijosanjima-cho, Tokushima 770, Japan

[1] Department of Chemistry, Faculty of Science, Hiroshima University, Kagamiyama, Higashihiroshima 724, Japan

[2] Institut für Physikalische Chemie, Technische Hochschule Darmstadt, Petersenstr. 20, D-64287 Darmstadt, Germany

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The ^{81}Br NQR triplet spectrum of $(CH_3CH_2NH)_3^{\oplus}(HgBr_3)^{\ominus}$ was measured in the range 77 K to near the m.p. (99 ~ 106 °C). ν_1 decreases strongly with increasing temperature, exhibiting 136.784 MHz at 77 K and 128.129 MHz at 298 K. ν_2 decreases from 82.060 MHz at 77 K to 76.322 MHz at 298 K. ν_3 increases with temperature, showing $\nu_3 = 81.292$ MHz at 77 K and 84.903 MHz at 298 K. Replacement of the ammonium hydrogens by deuterium produces a negative shift of ν_1 and positive ones of ν_2 and ν_3 at high temperatures. These shifts change with temperature from $|\sim 0|$ up to $|\sim 200|$ kHz.

The crystal structure of the title compound was determined at room temperature: $P2_1/m$, $Z = 2$, $a = 1021.6(8)$ pm, $b = 643.0(6)$ pm, $c = 691.8(6)$ pm, $\beta = 96.96(4)°$. The coordination of the mercury atom by the bromines is trigonal bipyramidal; by formation of bridges Hg $\cdots$ Br $\cdots$ Hg by one of the three bromines ($Br^{(2)}$) of the planar $HgBr_3^{\ominus}$ ions a double chain of trigonal bipyramids is formed, running along the *b*-axis of the crystal. $Br^{(1)}$ and $Br^{(3)}$ are single bonded to Hg. The hydrogen bonds $N-H \cdots Br^{(2)}$ and $N-H \cdots Br^{(3)}$ (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, ^{81}Br NQR, $^1H-^2D$ isotope effect, H-bonding.

Introduction

Studying the literature one may conclude that the tendency of $Hg_mX_n^{(n-2m)\ominus}$ (X = Cl, Br, I) anions to polymerize in the solid state of $A_1Hg_mX_n$ salts is much less pronounced than in the corresponding Cd salts. Halogenomercurate anions $(HgX_3)^{\ominus}$, $(HgX_4)^{2\ominus}$, $(Hg_2X_5)^{\ominus}$ and $(HgX_6)^{4\ominus}$ are often reported. The structure of $AHgX_3$ depends on the respective cations and halogens. As the cation becomes larger and the electronegativity of the halogen smaller, the polymerization seems to become less pronounced. $NaHgCl_3$ [1] crystallizes with a Perovskite NH_4CdCl_3-type structure. In contrast, in $(CH_3)_4NHgI_3$ [2] discrete pyramidal $HgX_3^{\ominus}$ ions loosely connected into chains are found. Another tendency is the coordination of the Hg atom. The Cl atom tends to like a linear two-coordination. NH_4HgCl_3 [3] contains distorted $HgCl_6$ 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 Körfer et al. [4] found that in orthorhombic $(CH_3NH_3)HgBr_3$ completely planar $HgBr_3^{\ominus}$ ions exist and two extra Hg $\cdots$ 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 $\cdots$ H–Y, etc., information on phase transitions and on the lattice dynamics becomes available. The ^{81}Br and ^{127}I NQR spectrum of

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Reprint requests to Dr. Hiromitsu Terao, Faculty of Integrated Arts and Sciences, Tokushima University, Minamijosanjima-cho, Tokushima 770, Japan.

$(CH_3NH_3)HgBr_3$ and $(CH_3NH_3)HgI_3$, respectively, was extensively studied as function of T by Terao and Okuda [5] who observed phase transitions in both systems and compared the room temperature structure of both compounds [4] with the NQR results. $(CH_3NH_3)_2HgBr_4$ (and $(CH_3ND_3)_2HgBr_4$) and $(CH_3NH_3)_2HgI_4$ have been studied by ^{81}Br and ^{127}I NQR, respectively, as a function of temperature by Terao et al. [6] and discussed in comparison with the crystal structure of the compounds [7] and their lattice dynamics [8].

It therefore was decided to study such salts by combination of NQR and X-ray diffraction. In the following we report on ^{81}Br NQR and the crystal structure of ethylammonium tribromomercurate(II), $(CH_3CH_2NH_3)^{\oplus}(HgBr_3)^{\ominus}$. ^{81}Br NQR is also reported for the partially deuterated analogue $(CH_3CH_2ND_3)^{\oplus}(HgBr_3)^{\ominus}$.

Experimental

The title compound was prepared from a dilute hydrobromic acid solution (or a methanol-acetone solution) containing stoichiometric amounts of $HgBr_2$ and $CH_3CH_2NH_3Br$. $CH_3CH_2NH_3Br$ was obtained by adding hydrobromic acid to an aqueous $CH_3CH_2NH_2$ 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 $(CH_3CH_2ND_3)^{\oplus}HgBr_3^{\ominus}$ was prepared by mixing $CH_3CH_2ND_3Br$ and $HgBr_2$ in a dilute D_2O solution of DBr where $CH_3CH_2ND_3Br$ was prepared from repeated cycles of dissolution of $CH_3CH_2NH_3Br$ ($CH_3CH_2ND_3Br$) in D_2O and successive evaporation of D_2O. The preparation of the D compounds were done under an atmosphere of N_2 in a glove bag. For the X-ray diffraction experiments, small single crystals were selected.

The ^{81}Br 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 C_{2h}^2-$P2_1/m$, 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, $\beta=96.96(4)°$. In Table 1 some crystallographic data are. In Table 2 we have listed the atomic coordinates and the thermal parameters. Table 3 contains intra- und interionic 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 $(CH_3CH_2NH_3)^{\oplus}(HgBr_3)^{\ominus}$. Diffractometer: Stoe-Stadi 4; wavelength: 71.069 pm (MoK_{α}); Monochrometer: Graphite (002); Scan $\omega/2\theta$. $M=486.3$.

Crystal habit	colorless, plates
Size/(mm)^3	$0.1 \times 0.3 \times 1.7$
Absorption coeff. (μ/m^{-1})	30145
$(\sin\theta/\lambda)_{max} \times 10^5$/pm	0.0054
Reflexions measured:	1337
Symmetry independent	651
Considered	651
Number of free parameters	52
F(000)	424
R(F)	0.058
R_w(F)	0.053
R_m(F)	0.057
Lattice constants a/pm	1021.6(8)
b/pm	643.0(6)
c/pm	691.8(6)
β/°	96.96(4)
$V_{Ucell} \times 10^{-6}$/(pm)^3	451.1(11)
Space group	$C_{2h}^2 - P2_1/m$
Formula units/Unit cell Z	2
ϱ_{calc}/mg · m^{-3}	3.58(1)
ϱ_{obs}/mg · m^{-3}	3.58(1)
Point positions	Atoms Hg, $Br^{(1)}$, $Br^{(2)}$, $Br^{(3)}$, $C^{(1)}$, $C^{(2)}$, N, $H^{(C2,1)}$, $H^{(N,1)}$ in 2(e): x, 1/4, z; $\bar{x}$, 3/4, $\bar{z}$.; $H^{(C1)}$, $H^{(C2,2)}$, $H^{(N,2)}$ in 4f: x, y, z; $\bar{x}$, $\bar{y}$, $\bar{z}$; $\bar{x}$ $1/2+y$, $\bar{z}$; x, $1/2-y$, z.

Table 2. Positional and thermal parameters of the atoms in the unit cell of $(CH_3CH_2NH_3)^{\oplus}(HgBr_3)^{\ominus}$. The temperature factor is of the form $T=\exp(-2^2 \cdot (U_{11} h^2 a^{*2} + U_{22} k^2 b^{*2} + U_{33} \cdot l^2 c^{*2} + 2 U_{12} hk a^* b^* + 2 U_{13} h \cdot l a^* c^* + 2 U_{23} kl b^* c^*))$. 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.

Atom	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	U_{13}
Hg	0.1376(1)	0.7500	0.5909(2)	461(9)	671(10)	559(10)	78(7)
$Br^{(1)}$	0.3537(4)	0.7500	0.4707(6)	477(22)	920(28)	630(25)	103(20)
$Br^{(2)}$	0.1033(3)	0.2500	0.5733(4)	463(21)	405(17)	447(19)	−49(16)
$Br^{(3)}$	0.1285(4)	0.7500	0.9620(5)	680(25)	505(20)	385(20)	−4(17)
N	0.2106(30)	0.2500	0.1204(39)	790(231)	563(178)	440(177)	182(169)
$C^{(1)}$	0.3536(36)	0.2500	0.1390(56)	423(245)	979(326)	822(305)	−118(225)
$C^{(2)}$	0.4037(34)	0.2500	−0.0602(60)	260(214)	1284(372)	788(308)	84(211)
$H^{(N,1)}$	0.1953(228)	0.2500	0.2723(97)	600			
$H^{(N,2)}$	0.1598(175)	0.1198(197)	0.0464(173)	600			
$H^{(C1)}$	0.4243(45)	0.3260(204)	0.2447(81)	600			
$H^{(C2,1)}$	0.5075(46)	0.2500	−0.0061(177)	600			
$H^{(C2,2)}$	0.3774(73)	0.1057(148)	−0.1350(248)	600			

Table 3. Intra- and interatomic distances and angles in the structure of $(CH_3CH_2NH_3)^{\oplus}(HgBr_3)^{\ominus}$. 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–$H^{(N)}$, H–C–H, and H–N–H are calculated on the basis of the symmetry, ideal tetrahedral angle, and $d(C-H)=d(N-H)=108$ pm, see text.

Connection	d/pm	Connection	angle/°
$HgBr_5$-Polyhedron			
$Hg-Br^{(1)}$	245.2(4)	$Br^{(1)}-Hg-Br^{(2)}$	134.4(1)
$Hg-Br^{(2)}$	258.2(4)	$Br^{(1)}-Hg-Br^{(3)}$	118.7(1)
$Hg-Br^{(2)\prime}$	323.5(3)	$Br^{(1)}-Hg-Br^{(2)\prime\,a}$	94.9(1)
$Hg-Br^{(3)}$	258.0(4)	$Br^{(2)}-Hg-Br^{(3)}$	106.9(1)
		$Br^{(2)\prime}-Hg-Br^{(2)\prime\prime\,b}$	167.4(1)
		$Br^{(2)\prime}-Hg-Br^{(3)}$	91.2(1)
		$Br^{(2)}-Hg-Br^{(2)\prime}$	83.7(1)
		$Hg-Br^{(2)\prime}-Hg^{\prime\,c}$	167.4(1)
		$Hg-Br^{(2)\prime}-Hg^{\prime\prime\,d}$	96.3(1)
Cation			
$C^{(1)}-C^{(2)}$	152.7(50)	$C^{(2)}-C^{(1)}-N$	111.4(25)
$C^{(1)}-N$	145.5(39)		
Hydrogen bond scheme			
$N-H^{(N,1)} \cdots Br^{(2)}$	344.2(25)	$N-H^{(N,1)} \cdots Br^{(2)\prime}$	165.3(18)
$H^{(N,1)} \cdots Br^{(2)}$	239(64)		
$N-H^{(N,2)} \cdots Br^{(3)}$	346.7(11)	$N-H^{(N,2)} \cdots Br^{(3)\prime\,e}$	154.6(15)
$H^{(N,1)} \cdots Br^{(3)}$	246(91)		
van der Waals distances			
$N \cdots Br^{(1)}$	418.2(20)		
$Br^{(1)} \cdots Br^{(1)}$	437.5(5)		
$Br^{(3)} \cdots Br^{(3)}$	422.3(5)		
$Br^{(1)} \cdots C^{(1)}$	377.8(34)		
$Br^{(2)} \cdots C^{(2)}$	375.0(39)		
$Br^{(1)} \cdots C^{(2)}$	394.2(23)		
$C^{(2)} \cdots C^{(2)}$	377.9(50)		

[a] $Br^{(2)\prime}$: $-x$, $1/2-y$, $1-z$; [b] $Br^{(2)\prime\prime}$: $-x$, $1+y$, $1-z$; [c] Hg': x, $y-1$, z; [d] Hg'': $-x$, $1-y$, $1-z$; [e] $Br^{(3)\prime}$: x, $y-1$, $z-1$.

bipyramids $HgBr_5$ run along [010] at $x=0$. The cations $(CH_3CH_2NH_3)^{\oplus}$ are inserted between these chains, and hydrogen bonds N–H ··· Br connect the double chains in the *c* direction to *bc* planes. This is seen by looking at Fig. 2, which shows the projection of the unit cell along [010] onto the *ac* plane.

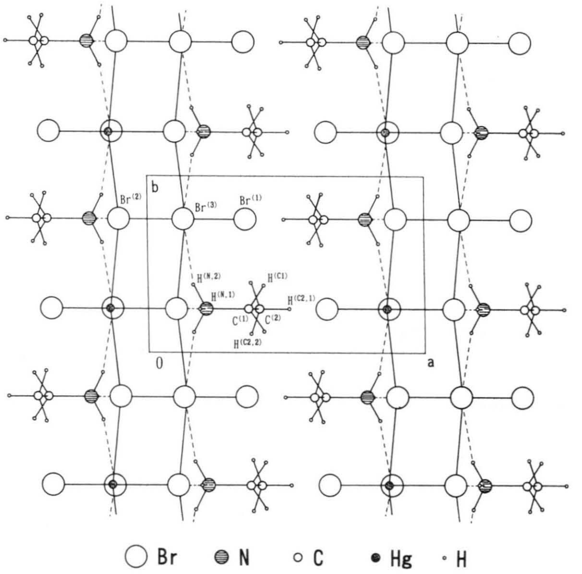

Fig. 1. Projection of the unit cell of $(CH_3CH_2NH_3)^{\oplus}(HgBr_3)^{\ominus}$ along *c* onto the *ab* plane. The hydrogen bonds N–H ··· Br are marked by dashed lines.

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 CH_2 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 $H^{(C1,1)}$ and $H^{(C1,2)}$ given in Table 3. With the same argument we have determined

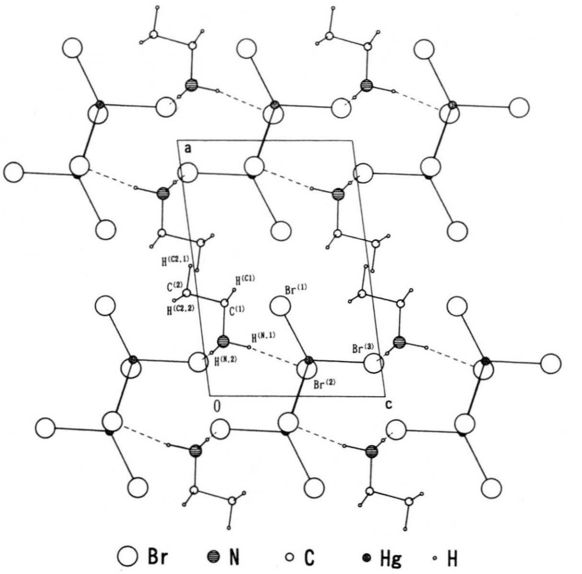

Fig. 2. Projection of the unit cell of $(CH_3CH_2NH_3)^\oplus (HgBr_3)^\ominus$ along the 2_1 axis onto the *ac* plane. The hydrogen bonds N–H ··· Br are marked by dashed lines.

Table 4. ^{81}Br NQR frequencies of $(CH_3CH_2NH_3)^\oplus(HgBr_3)^\ominus$ (H) and $(CH_3CH_2ND_3)^\oplus(HgBr_3)^\ominus$ (D) at selected temperatures.

T/K		ν/MHz^a		$\nu^D - \nu^H$/MHz^b
		H	D	
77	ν_1	136.784(55)	136.758(57)	−0.026
	ν_2	82.060(11)	82.257(19)	0.197
	ν_3	81.292(18)	81.298(36)	0.006
298	ν_1	128.129(39)	128.045(43)	−0.084
	ν_2	76.322(32)	76.483(20)	0.161
	ν_3	84.903(40)	85.088(38)	0.185

[a] Numbers in parentheses are signal to noise ratios observed on a recorder. [b] Deuteration shifts.

the positions of the hydrogen atoms of the group $C^{(2)}H_3$. We fix the atom $H^{(C2,1)}$ at the point position 2(e) with constraint for d(C–H) and ∠(H–C–H). The same arguments and the same procedure is applied to the NH_3 group for $H^{(N,1)}$ in 2(e), and $H^{(N,2)}$ and $H^{(N,3)}$ in 4(f).

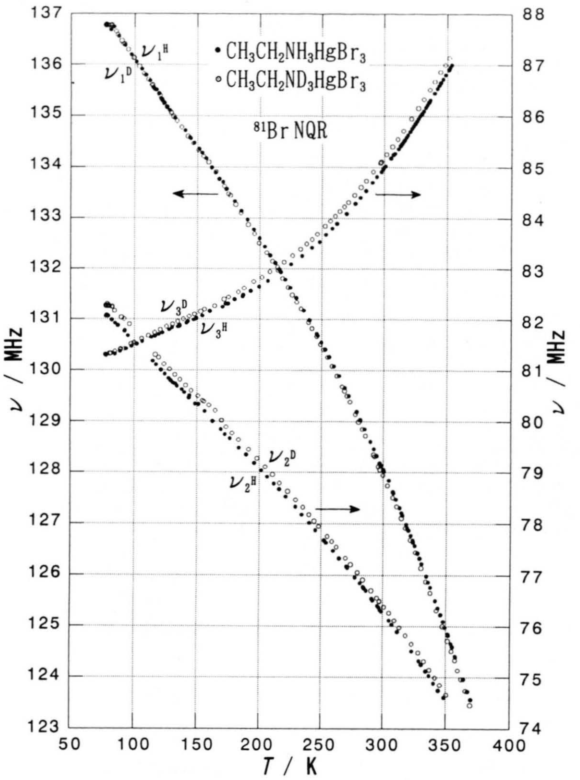

Fig. 3. Frequencies of the ^{81}Br NQR spectrum of $(CH_3CH_2NH_3)^\oplus(HgBr_3)^\ominus$ as a function of temperature. The open circles correspond to the ^{81}Br NQR spectrum of $(CH_3CH_2ND_3)^\oplus(HgBr_3)^\ominus$.

The ^{81}Br NQR spectrum is a triplet with some unusual features. The frequencies ν_i of both protonated and deuterated salts are plotted as a function of T in Figure 3. At $T = 77$ K ν_1 is by a factor of 1.7 higher than ν_3 in frequency. At 77 K ν_2 and ν_3 differ little. However the temperature coefficient $d\nu/dT$ is positive for ν_3, opposite to those of ν_1 and ν_2. In Table 4 frequencies at selected temperatures are reported. By deuteration all lines are affected in their frequency up to ~|200| kHz. The sign of the shifts of ν_2 and ν_3 is opposite to that of ν_1.

Discussion

$(CH_3CH_2NH_3)^\oplus(HgBr_3)^\ominus$ is an ionic salt. For the discussion we adopt the atomic (ionic, van der Waals) radii $r(NH_3^\oplus) = 163$ pm, $r(Br^\ominus) = 196$ pm, and within distances of N ··· Br $\leqq 360$ pm we have to discuss hydrogen bonds N–H ··· Br. $r_{vdw}(Br) = 185$ pm, $r_{vdw}(CH_2, CH_3) = 170$ 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.

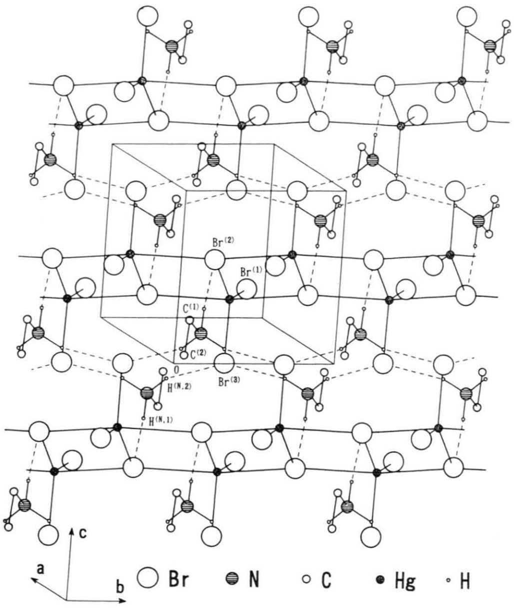

Fig. 4. Unit cell of $(CH_3CH_2NH_3)^{\oplus}(HgBr_3)^{\ominus}$.

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 $HgBr_3^{\ominus}$ 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 $HgBr_3^{\ominus}$ ion with two nearly equal distances Hg–Br of 258 pm, $d(\text{Hg–Br}^{(2)})$ and $d(\text{Hg–Br}^{(3)})$ and a shorter distance $d(\text{Hg–Br}^{(1)}) = 245$ pm. The angles Br–Hg–Br are grouped around 120° with deviations of ±15°, see Table 3. Two atoms $\text{Br}^{(2)}$ of neighboring $HgBr_3^{\ominus}$ ions are coordinated with each $HgBr_3^{\ominus}$, 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 $d(\text{N} \cdots \text{Br}) \leqq 360$ 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 $d(\text{N} \cdots \text{Br}^{(2)})$: 344 pm and two $d(\text{N} \cdots \text{Br}^{(3)})$: 347 pm. $d(\text{N} \cdots \text{Br}^{(1)})$ is quite long (419 pm) and we can not expect a hydrogen bond $\text{N–H} \cdots \text{Br}^{(1)}$.

In Table 3 we have listed the distances and angles of the hydrogen bond network. $\text{Br}^{(2)}$ is connected with the cation by one hydrogen bond, and $\text{Br}^{(3)}$ 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).

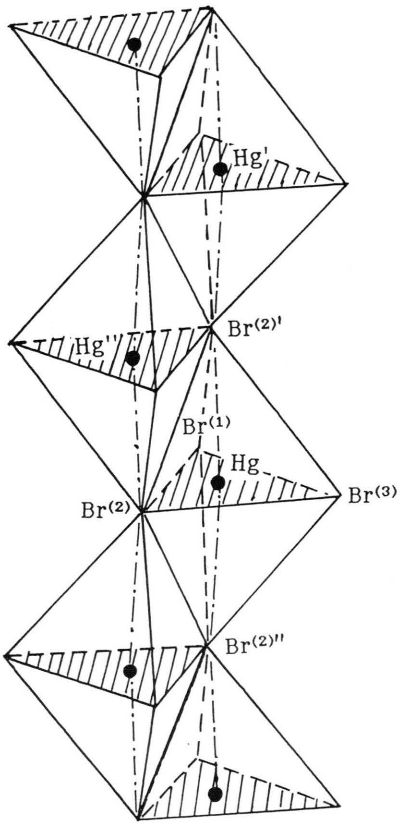

Fig. 5. The trigonal bipyramidal coordination of $HbBr_5$ as the unit of the double chain anion (cf. Table 3).

The present structure is compared with that of $(CH_3NH_3)^{\oplus}(HgBr_3)^{\ominus}$ [4] in which the pyramidal configuration around the Hg atom of planar $(HgBr_3)^{\ominus}$ and the double chain are found too. Due to a small size and higher symmetry of $(CH_3NH_3)^{\oplus}$, the $(CH_3NH_3)^{\oplus}$ 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 $\text{Hg–Br}_{\text{bridging}}$ bonds are along the *b* axis such that two terminal Br atoms are equivalent. The bond distances $\text{Hg–Br}_{\text{terminal}} = 252.7$, $\text{Hg–Br}_{\text{bridging}} = 256.5$ in

$(HgBr_3)^{\ominus}$, and Hg ··· $Br_{bridging} = 319.2$ pm as an intermolecular bond are compared to the corresponding values in Table 3. The H-bonds N–H ··· Br are expected only for the terminal Br atoms with d(N ··· 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 $(CH_3NH_3)^{\oplus}$ salt.

In the ^{81}Br NQR spectrum, ν_1 is much higher than ν_2 and ν_3. From the theory of nuclear quadrupole interaction the most simple relation is that the frequency dependence on the bond distance d(Hg–Br) should be $\nu = a \cdot 1/d(\text{Hg-Br})^3$. Therefore it is correct if we assign ν_1 to $Br^{(1)}$ because $d(\text{Hg-Br}^{(1)})$ 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 ν_1. Furthermore, $Br^{(1)}$ is neither affected by a hydrogen bond nor is it involved in a bridging configuration Hg–Br–Hg. Also the temperature dependence of ν_1 is as one expects from the Bayer theory [14]. ν_3 increases with increasing temperature. Therefore Φ_{zz} 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. $Br^{(2)}$ is incorporated into one H-bond and a Hg–Br–Hg bridging bond, while $Br^{(3)}$ 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 $\nu_3 \leftrightarrow Br^{(3)}$ and consequently the assignment $\nu_2 \leftrightarrow Br^{(2)}$. The observation [5] that $d\nu/dT$ of bridging Br atoms in the $(CH_3NH_3)^{\oplus}$ salt is also negative seems to support the above assignment. Further, the signal intensity of ν_2 is weaker than ν_3 (Table 4). The bridging Br atom in the $(CH_3NH_3)^{\oplus}$ salt shows also a weaker intensity than the terminal Br atom (which is incorporated into the H-bonds scheme). The assignment $\nu_i \leftrightarrow Br^{(j)}$ 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 $(CH_3NH_3)^{\oplus}$ salt to the $(CH_3CH_2NH_3)^{\oplus}$ salt the frequency range of the ^{81}Br NQR spectrum is widened by ca. a factor three: For the $(CH_3NH_3)^{\oplus}$ 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 ··· Hg intermolecular bonding in the two compounds change the negative charges on the respective Br atoms of $(HgBr_3)^{\ominus}$, so that their total net charges remain constant.

Frequency lowering in ν_2 and ν_3 (and resultant raising in ν_1) from the mean values may mostly be ascribed to the H-bonding and Hg ··· 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 ··· $Br^{(2)}$–Hg is 96.3°. For H-bonds we obtain: $H^{(N,1)}$ ··· $Br^{(2)}$–Hg = 94.1°, $H^{(N,2)}$ ··· $Br^{(3)}$–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].

$\nu(T)$ curves show no evidence of phase transition in the $(CH_3CH_2NH_3)^{\oplus}$ salt from 77 K up to near the m.p. (99 ~ 106 °C). The successive phase transitions observed in the $(CH_3NH_3)^{\oplus}$ salt [5] are tentatively ascribed exclusively to the motion of the $(CH_3NH_3)^{\oplus}$ ion having a more symmetrical shape compared to the ethyl ammonium ion.

The frequency shifts produced by deuteration are similar to those observed in $(CH_3NH_3)_2HgBr_4$ [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 ··· Br–Hg ~ 90°, then we expect positive shifts at high temperatures and negative shifts at a low temperature limit. If H ··· Br–Hg ~ 180°, the reverse shifts may be expected. With $H^{(N,2)}$ ··· $Br^{(3)}$–Hg = 102.5°, the shifts of ν_3 seem to coincide with the above prediction. The shifts are positive at high temperatures and become almost zero around 77 K. With $H^{(N,1)}$ ··· $Br^{(2)}$–Hg = 94.1°, the shifts of ν_2 are also positive at high temperatures, but in contradiction to the above prediction their values tend to increase with decreasing temperature. Further, for ν_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 additional explanation in which cationic motions possibly take part. It may also be helpful to investigate the isotope-effects in a series of alkylammonium halogenomercurates and to classify the types of effects.

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