

## Structure Determination of Methylammonium Bromomercurates(II): $[(\text{CH}_3)_3\text{NH}]\text{HgBr}_3$ and $[(\text{CH}_3)_2\text{NH}_2]_2\text{HgBr}_4$

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### Abstract

The crystal structures of two methylammonium bromomercurates(II),  $[(\text{CH}_3)_3\text{NH}]\text{HgBr}_3$  and  $[(\text{CH}_3)_2\text{NH}_2]_2\text{HgBr}_4$ , were determined by single-crystal X-ray diffraction. Different coordination of mercury is observed. In  $[(\text{CH}_3)_3\text{NH}]\text{HgBr}_3$ , chains of trigonal almost planar  $[\text{HgBr}_3]^-$  units with Hg—Br distances between 2.516 (1) and 2.573 (1) Å and angles close to 120° are parallel to *a*. Isolated distorted tetrahedra are found for the other compound with Hg—Br distances between 2.569 (1) and 2.650 (1) Å in  $\text{HgBr}_4^{2-}$  units. The methylammonium groups are connected by hydrogen bridges to the bromine atoms. A bifurcated hydrogen bridge is observed for  $[(\text{CH}_3)_2\text{NH}_2]_2\text{HgBr}_4$ . A detailed review of crystal structures of several compounds containing Hg and Br reveals different Hg coordination types and a classification of Hg—Br bond lengths is discussed in terms of a correlation diagram. Crystal data: trimethylammonium tribromomercurate,  $[(\text{CH}_3)_3\text{NH}]\text{HgBr}_3$ ,  $M_r = 518.45$ , monoclinic,  $P2_1/a$ ,  $Z = 4$ ,  $F(000) = 880$ ,  $\lambda(\text{Ag } K\alpha) = 0.5609$  Å,  $T = 297$  (1) K,  $a = 8.080$  (2),  $b = 14.583$  (2),  $c = 8.825$  (1) Å,  $\beta = 90.98$  (2)°,  $V = 1039.6$  (9) Å<sup>3</sup>,  $D_x = 3.298$  Mg m<sup>-3</sup>,  $\mu = 14.2$  mm<sup>-1</sup>,  $R = 0.031$ ,  $wR = 0.046$  for 1149 observed independent reflections; bis(dimethylammonium) tetrabromomercurate,  $[(\text{CH}_3)_2\text{NH}_2]_2\text{HgBr}_4$ ,  $M_r = 612.41$ , monoclinic,  $P2_1/n$ ,  $Z = 4$ ,  $F(000) = 1096$ ,  $\lambda(\text{Ag } K\alpha) = 0.5609$  Å,  $T = 297$  (1) K,  $a = 8.209$  (3),  $b = 11.778$  (3),  $c = 15.269$  (8) Å,  $\beta = 94.42$  (4)°,  $V = 1471.9$  (9) Å<sup>3</sup>,  $D_x = 2.745$  Mg m<sup>-3</sup>,  $\mu = 11.4$  mm<sup>-1</sup>,  $R = 0.041$ ,  $wR = 0.041$  for 1575 observed independent reflections.

### Introduction

Double salts formed by the reaction of substituted ammonium halides and metal halides exhibit successive phase transitions owing to the rearrangement of

the substituted ammonium groups. Some of these transitions are furthermore related to physical properties. The general formulae of this class of compounds may be written as  $R_x\text{NH}_{4-x}\text{MX}_3$  and  $(R_x\text{NH}_{4-x})_2\text{MX}_4$  with  $R = \text{alkyl or aryl}$ ,  $M = \text{divalent metal ion (Hg, Cu, Mn, Cd, . . .)}$ ,  $X = \text{Br, Cl, I}$ , and  $x = 1, 2, 3, 4$ .

Among the halogenomercurates  $\text{CH}_3\text{NH}_3\text{HgCl}_3$  especially has been studied extensively (Ben Salah, Bats, Kalus, Fuess & Daoud, 1982; Fuess, Körfer, Arend & Kind, 1985). A ferro–paraelectric first-order phase transition in this compound was examined by diffraction, thermoanalysis and spectroscopy. Moreover, the crystal structures of different monomethyl- (Körfer, Fuess, Bats & Klebe, 1985; Körfer, Fuess & Bats, 1986), dimethyl- (Ben Salah, Bats, Fuess & Daoud, 1982) and trimethyl- (Ben Salah, Bats, Fuess & Daoud, 1983) ammonium halogenides have been determined. Existing chloromercurate structures have been presented in the form of a correlation diagram (Ben Salah *et al.*, 1983) in order to obtain a common view of the various geometries found in the environment of mercury(II).

### Experimental

Single crystals of the title compounds were obtained by slow evaporation of stoichiometric solutions of the substituted ammonium and mercury bromides in a mixture of acetone and methanol.  $(\text{CH}_3)_2\text{NH}_2\text{Br}$  and  $(\text{CH}_3)_3\text{NHBr}$  were produced from an exothermal reaction of HBr with  $(\text{CH}_3)_2\text{NH}$  and  $(\text{CH}_3)_3\text{N}$ , respectively. Both compounds were examined by differential scanning calorimetry (DSC) using a Mettler device in the temperature range 120 to 420 K. Two peaks (273.6 and 333.3 K) were observed for  $[(\text{CH}_3)_2\text{NH}_2]_2\text{HgBr}_4$  indicating possible phase transitions.

Data for structure determinations were collected on an Enraf–Nonius CAD-4 diffractometer at room temperature with Ag  $K\alpha$  radiation (graphite monochromator). Lattice constants were obtained from setting angles of 25 reflections. Experimental details are listed in Table 1.

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Table 1. *Experimental conditions, crystal data and refinement*

	$[(\text{CH}_3)_3\text{NH}]\text{HgBr}_3$	$[(\text{CH}_3)_2\text{NH}_2]\text{HgBr}_4$
Scan type	$\omega$	$\omega$
Scan range $h$	0 $\rightarrow$ 9	0 $\rightarrow$ 10
$k$	-17 $\rightarrow$ 17	0 $\rightarrow$ 14
$l$	-10 $\rightarrow$ 10	-18 $\rightarrow$ 18
$\sin(\theta/\lambda)_{\text{max}}$ ( $\text{\AA}^{-1}$ )	0.58	0.61
Crystal size (mm)	0.06 $\times$ 0.1 $\times$ 0.32	0.15 $\times$ 0.4 $\times$ 0.45
No. of reflections (measured)	3872	3458
Reflections with $I > 3\sigma(I)$	1702	2801
No. of variables	74	101
$S$	1.90	1.57

Data were corrected for Lorentz-polarization effects. The structures were solved by Patterson and Fourier techniques and direct methods, and refined in least-squares calculations. All calculations were performed with the *SDP* program package (B. A. Frenz & Associates, Inc., 1982) on a PDP11/34 computer or with the *SHELX76* and *SHELXS* program systems (Sheldrick, 1976, 1986) on a UNIVAC 1108 computer.

A summary of the experimental conditions is given in Table 1. Atomic scattering factors and anomalous-dispersion values were taken from *International Tables for X-ray Crystallography* (1974). The positional and thermal parameters of the atoms are given in Table 2.\*

### $[(\text{CH}_3)_3\text{NH}]\text{HgBr}_3$

Crystals were colourless, reflections were measured in a hemisphere of reciprocal space up to  $2\theta = 38^\circ$ . Three standard reflections showed intensity increases of about 1.8%. All reflections were rescaled accordingly. The data were corrected empirically for absorption effects, by  $\psi$  scans of three reflections (North, Phillips & Mathews, 1968); relative transmission 0.57–1.00. Equivalent reflections were averaged ( $R_{\text{int}} = 0.027$ ).

An attempt to determine the structure by Patterson techniques did not produce a unique solution. Additional calculations by direct methods lead to the localization of the four independent heavy atoms. A difference Fourier synthesis yielded the trimethylammonium groups. All atoms were refined with anisotropic thermal parameters by least-squares methods. An extinction coefficient  $g$  according to  $|F_o| = |F_c|/(1 + gI_c)$  was included in the refinement and  $g = 1.29 \times 10^{-7}$  was obtained. No hydrogen atoms could be located from the Fourier map. All positions were calculated, based on C—H and N—H distances of 0.95  $\text{\AA}$  and tetrahedral angles. They were

Table 2. *Positional and thermal parameters, with e.s.d.'s in parentheses*

$U_{\text{eq}} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$ . Values for hydrogen were not refined.

	$x$	$y$	$z$	$U_{\text{eq}}$ or $U_{\text{iso}}(\text{\AA}^2)$
$[(\text{CH}_3)_3\text{NH}]\text{HgBr}_3$				
Hg(1)	0.14532 (9)	0.28703 (4)	0.27080 (7)	0.0619 (1)
Br(1)	0.1722 (2)	0.4562 (1)	0.3209 (2)	0.0593 (5)
Br(2)	-0.0597 (2)	0.2325 (1)	0.0639 (2)	0.0612 (5)
Br(3)	0.2538 (2)	0.1706 (1)	0.4592 (2)	0.0622 (5)
N(1)	0.744 (2)	0.0475 (9)	0.740 (1)	0.056 (4)
C(1)	0.636 (3)	0.130 (1)	0.754 (2)	0.081 (6)
C(2)	0.753 (3)	-0.000 (1)	0.875 (2)	0.103 (8)
C(3)	0.912 (2)	0.076 (2)	0.686 (2)	0.100 (6)
H(1)	0.694	0.006	0.667	0.08
H(2)	0.628	0.162	0.659	0.10
H(3)	0.527	0.112	0.783	0.10
H(4)	0.680	0.171	0.829	0.10
H(5)	0.827	-0.055	0.864	0.11
H(6)	0.805	0.035	0.954	0.11
H(7)	0.652	-0.023	0.908	0.11
H(8)	0.983	0.025	0.677	0.11
H(9)	0.902	0.106	0.591	0.11
H(10)	0.961	0.118	0.758	0.11
$[(\text{CH}_3)_2\text{NH}_2]\text{HgBr}_4$				
Hg(1)	0.28690 (7)	0.29536 (1)	0.05088 (4)	0.0493 (1)
Br(1)	0.2882 (2)	0.5146 (1)	0.0593 (1)	0.0636 (4)
Br(2)	0.0220 (2)	0.2076 (1)	0.0979 (1)	0.0751 (5)
Br(3)	0.3280 (2)	0.2280 (1)	-0.1111 (1)	0.0599 (5)
Br(4)	0.5451 (2)	0.2175 (1)	0.1400 (1)	0.0626 (5)
N(1)	0.735 (1)	0.1770 (9)	0.9280 (9)	0.073 (4)
N(2)	0.294 (2)	0.517 (1)	0.8320 (8)	0.072 (4)
C(1)	0.805 (2)	0.207 (1)	0.846 (1)	0.108 (6)
C(2)	0.718 (2)	0.054 (1)	0.947 (2)	0.109 (8)
C(3)	0.377 (2)	0.492 (1)	0.7524 (9)	0.070 (5)
C(4)	0.115 (2)	0.513 (1)	0.825 (1)	0.075 (5)
H(1)	0.629	0.212	0.928	0.06
H(2)	0.802	0.211	0.976	0.06
H(3)	0.329	0.592	0.853	0.06
H(4)	0.335	0.465	0.878	0.06

Table 3. *Bond distances ( $\text{\AA}$ ) and angles ( $^\circ$ ), with e.s.d.'s in parentheses*

	$[(\text{CH}_3)_3\text{NH}]\text{HgBr}_3$	$[(\text{CH}_3)_2\text{NH}_2]\text{HgBr}_4$
Hg—Br(1)	2.517 (1)	2.588 (1)
Br(2)	2.570 (1)	2.569 (1)
Br(3)	2.525 (1)	2.650 (1)
Br(4)		2.603 (1)
Br(1)—Hg—Br(2)	118.75 (5)	112.87 (5)
Br(1)—Hg—Br(3)	121.07 (4)	110.24 (4)
Br(1)—Hg—Br(4)		109.01 (5)
Br(2)—Hg—Br(3)	118.19 (3)	108.34 (5)
Br(2)—Hg—Br(4)		112.90 (5)
Br(3)—Hg—Br(4)		103.02 (4)
N(1)—C(1)	1.489 (15)	1.469 (17)
C(2)	1.388 (17)	1.488 (15)
C(3)	1.508 (16)	
N(2)—C(3)		1.472 (14)
C(4)		1.476 (17)
C(1)—N(1)—C(2)	110.87 (1.07)	116.86 (1.06)
C(1)—N(1)—C(3)	109.82 (1.11)	
C(2)—N(1)—C(3)	111.78 (1.16)	
C(3)—N(2)—C(4)		117.34 (1.05)

not included in least-squares refinement. The final difference Fourier synthesis was featureless,  $(\Delta/\sigma)_{\text{max}} = 0.05$  in the last cycle of refinement.

### $[(\text{CH}_3)_2\text{NH}_2]\text{HgBr}_4$

Data of a colourless sample were collected in a quarter of reciprocal space up to  $2\theta = 40^\circ$  with an  $\omega$  scan. Three standard reflections were repeatedly

\* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52840 (17 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

remeasured during the data collection. No intensity change was observed for two standard reflections of medium intensity. The intensity of the strongest reflection, however, increased over the time of data collection, which was attributed to a decrease of extinction due to radiation damage. No correction for time stability was applied. All reflections were corrected empirically for absorption effects, by  $\psi$  scans of three reflections (North, Phillips & Mathews, 1968); relative transmission 0.34–1.00. The

equivalent reflections were averaged,  $R_{\text{int}} = 0.051$ . The structure was determined by Patterson and Fourier techniques in space group  $P2_1/n$  and refined by least-squares methods with anisotropic thermal parameters. As no hydrogen atoms were detected from a difference Fourier synthesis the positions of those bonded to the nitrogen atoms were calculated. The N—H distances were supposed to be 0.95 Å and the C—N—H angles 114.6°. In the least-squares refinement positions and thermal parameters of the hydrogen atoms were fixed. A final difference Fourier synthesis showed only one peak of about  $1.0 \text{ e } \text{Å}^{-3}$  near the mercury atom, but was otherwise featureless ( $0.8\text{--}0.5 \text{ e } \text{Å}^{-3}$ ),  $(\Delta/\sigma)_{\text{max}} = 0.03$  in the last cycle of refinement; an extinction parameter was finally refined to  $g = 2.9 \times 10^{-7}$ .

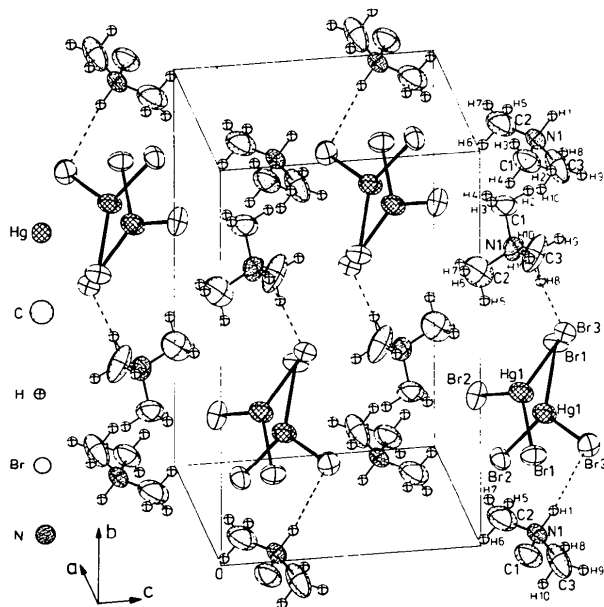


Fig. 1. Perspective view of the crystal structure of  $[(\text{CH}_3)_3\text{NH}]\text{HgBr}_3$ . Thermal ellipsoids are at the 50% probability level. Hydrogen bonds are indicated by broken lines.

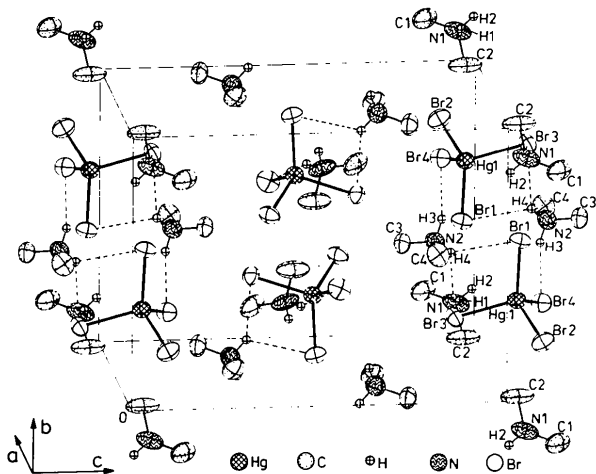


Fig. 2. Perspective view of the crystal structure of  $[(\text{CH}_3)_2\text{NH}_2]_2\text{HgBr}_4$ .

### Discussion

Bond distances and angles are given in Table 3, the structures are displayed in Figs. 1 and 2.

The main building block of the structure of  $[(\text{CH}_3)_3\text{NH}]\text{HgBr}_3$  is an almost planar  $[\text{HgBr}_3]^-$  unit. These units are interconnected *via*  $\text{Hg}\cdots\text{Br}$  bonds (Fig. 3) almost parallel to *a*. Distances are  $\text{Hg}\cdots\text{Br}(2) = 3.047(1)$  and  $\text{Hg}\cdots\text{Br}(3) = 3.660(1)$  Å.  $[(\text{CH}_3)_3\text{NH}]\text{HgBr}_3$  is not isotopic with the chlorine analogue (Ben Salah *et al.*, 1983). The main building units in the tetrahalogenomercurates(II)  $[(\text{CH}_3)_2\text{NH}_2]_2\text{HgX}_4$  with  $X = \text{Cl}, \text{Br}, \text{I}$  are isolated tetrahedra. The tetrahedra are heavily distorted for  $X = \text{Cl}$  and  $\text{Br}$  but are almost regular for the iodine compound.  $[(\text{CH}_3)_2\text{NH}_2]_2\text{HgBr}_4$  and  $[(\text{CH}_3)_2\text{NH}_2]_2\text{HgCl}_4$  (Ben Salah, Bats, Fuess & Daoud, 1982) are isostructural (space group  $P2_1/n$ ) with similar Hg coordination. The Hg—*X* distances increase from  $X = \text{Cl}$  [2.424(2)—2.530(2) Å] to  $X = \text{Br}$  [2.569(1)—2.650(1) Å] to  $X = \text{I}$  (2.767—2.797 Å) (Pabst, 1990).

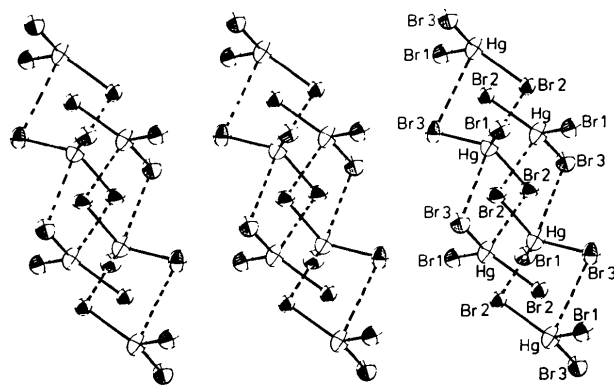


Fig. 3. Three parallel chains of  $[\text{HgBr}_3]^{3-}$  units, almost in the *a* direction, in  $[(\text{CH}_3)_3\text{NH}]\text{HgBr}_3$ .

Table 4. Hydrogen-bonding scheme ( $\text{\AA}$  and  $^\circ$ )

E.s.d.'s, given in parentheses, were calculated without hydrogen.

	H...Br	N...Br	N—H	N—H—Br
$(\text{CH}_3)_3\text{NH]HgBr}_3$				
N(1)—H(1)···Br(3)	2.85 (1)	3.640 (9)	0.964 (8)	139.8 (6)
$[(\text{CH}_3)_2\text{NH}_2]_2\text{HgBr}_4$				
N(1)—H(1)···Br(3)	2.52 (1)	3.41 (1)	0.963 (9)	155.3 (6)
N(1)—H(2)···Br(2)	2.50 (2)	3.39 (1)	0.97 (1)	153.4 (6)
N(2)—H(3)···Br(4)	2.47 (1)	3.41 (1)	0.97 (1)	161.5 (7)
Br(1)	2.90 (1)	3.48 (1)		119.6 (6)
N(2)—H(4)···			0.98 (1)	
Br(3)	2.80 (1)	3.53 (1)		132.3 (6)

### Hydrogen-bonding scheme

The crystal structures of double salts composed of  $\text{HgX}_2$  and alkylammonium halides are usually characterized by building units of  $\text{HgX}$  (isolated tetrahedra, chains, double chains) which are inter-

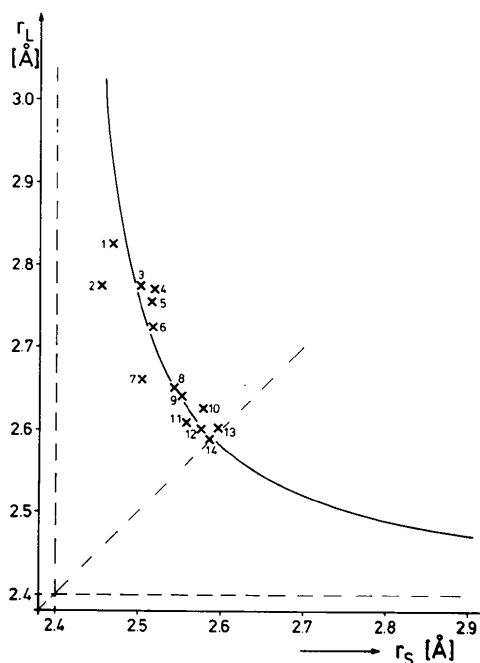


Fig. 4. Correlation diagram showing the average value of the longer Hg—Br bonds as a function of the average value of the shorter Hg—Br bonds for tetrahedral HgBr coordinations. References: 1,  $[\text{Mg}(\text{OH})_2][\text{Hg}_2\text{Br}_6]$  (Brodersen & Pezzeri, 1983); 2,  $(\text{C}_2\text{H}_5\text{N}_2\text{O})\text{HgBr}_2$  (Lechat, Francisco & Airoidi, 1980); 3,  $(\text{C}_{22}\text{H}_{31}\text{O}_2\text{S})\text{HgBr}$  (Terzis, Faught & Pouskoulelis, 1980); 4,  $\text{HgBr}_2 \cdot (\text{C}_2\text{H}_5)_2\text{PCH}_2\text{COOH}$  (Podlahová, Kratochvil, Loub & Paulus, 1986); 5,  $([\text{Ph}_3\text{AsO}]_2\text{H})(\text{Hg}_2\text{Br}_6)$  (Harris, Inglis & McKechnie, 1967); 6,  $[(\text{Cu}_2\text{Au})(\text{Budtc})_6](\text{Hg}_2\text{Br}_6)$  (Gal, Beurskens, Cras, Beurskens & Willems, 1976); 7,  $\text{C}_{10}\text{H}_{20}\text{N}_2\text{S}_4\text{HgBr}_2$  (Chieh, 1978b); 8,  $\text{C}_6\text{H}_{10}\text{O}_4\text{S}_4\text{HgBr}_2$  (Skol'nikova, Poraj-Košic, Djatlova, Zavodnik, Bel'skij & Podlaga, 1980); 9,  $\text{C}_{10}\text{H}_{20}\text{N}_2\text{S}_4\text{Hg}_2\text{Br}_2$  (Chieh, 1978a); 10,  $[(\text{CH}_3)_2\text{NH}_2]_2\text{HgBr}_4$  (this paper); 11,  $\text{Cs}_3\text{HgBr}_5$  (Pakhomov, Fedorov & Sadikov, 1978); 12,  $\text{Cs}_2\text{HgBr}_4$  (Pakhomov, Fedorova & Ivanova-Korfini, 1978); 13,  $(\text{CH}_3\text{NH}_2)_2\text{HgBr}_4$  (Körfer *et al.*, 1986); 14,  $[\text{N}(\text{CH}_3)_4]_2\text{HgBr}_4$  (Kamenar & Nagl, 1976).

connected by hydrogen bonds of the ammonium ions. The hydrogen-bonding scheme determined from calculated hydrogen positions is presented in Table 4.

Three out of the four hydrogen bonds between ammonium and Br in  $[(\text{CH}_3)_2\text{NH}_2]_2\text{HgBr}_4$  are fairly strong with N...Br distances of about 3.4  $\text{\AA}$ . The remaining one is bifurcated and the N...Br distances of about 3.5  $\text{\AA}$  classify this bond as rather weak. It is evident from inspection of Table 4 and the temperature factors of the dimethylammonium groups that the strong hydrogen bonds lead to reduction of the thermal motion of these groups. In  $[(\text{CH}_3)_3\text{NH}]\text{HgBr}_3$  only one hydrogen connected to N is involved in a weak hydrogen bond. Values for hydrogen bonds between N and Br range from 3.17  $\text{\AA}$  in  $\text{C}_5\text{H}_{11}\text{N} \cdot \text{BrH}$  to 3.70  $\text{\AA}$  in  $\text{N}_2\text{H}_5\text{Br}$ . The hydrogen bonds determined in the two title compounds are therefore of medium strength.

### Coordination of bromomercurates(II)

A great variety of Hg coordinations is observed in halogenomercurates(II) especially in chloromercurates. The coordination polyhedra are often classified as trigonal, tetrahedral, trigonal bipyramidal or

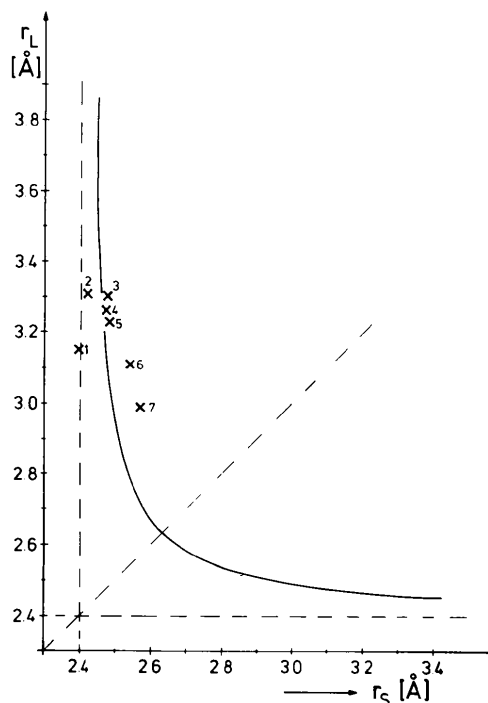


Fig. 5. Correlation diagram for octahedral HgBr coordinations. References: 1,  $\text{Hg}(\text{Cl}, \text{Br})_2$  (Scholten & Bijvoet, 1941); 2,  $\text{CH}_3\text{CN} \cdot 3\text{HgBr}_2$  (Leligny, Frey & Monier, 1972); 3,  $\text{C}_4\text{H}_8\text{O} \cdot \text{HgBr}_2$  (Frey, Leligny & Ledésert, 1971); 4,  $\text{KHgBr}_2 \cdot \text{CN} \cdot 2\text{H}_2\text{O}$  (Brodersen & Frohring, 1981); 5,  $\text{HgBr}_2$  (Braekken, 1932); 6,  $\text{Tl}_4\text{HgBr}_6$  (Brodersen, Thiele & Görz, 1973); 7,  $\text{Hg}_2\text{Br}_2$  (Ewald & Hermann, 1931).

octahedral and are mostly described as heavily distorted. In a previous paper (Ben Salah *et al.*, 1983) we reported an attempt to arrange all these observations in a diagram which correlates the observed distances with respect to  $\text{HgCl}_2$ . This molecule is linear with  $\text{Hg}-\text{Cl}$  distances of 2.252 Å and a  $\text{Cl}-\text{Hg}-\text{Cl}$  angle of  $180^\circ$  (Subramanian & Seff, 1980). Several other structures contain this unit more or less elongated and completed by additional chlorine atoms.

The tendency to form almost linear, isolated  $\text{HgX}_2$  units decreases from  $X = \text{Cl}$  to  $\text{I}$ . The most common coordination in bromo- and iodo-mercurates is tetrahedral but other types of coordination are also observed in the bromomercurates.

The correlation scheme for the classification of the  $\text{Hg}^{2+}$  coordination has now been extended to the  $\text{Hg}-\text{Br}$  bond. 32 bromomercurate structures have been compiled and a wide range of  $\text{Hg}-\text{Br}$  distances is observed. The lower limit ( $d$ ) is given by  $\text{HgBr}_2$  with an observed distance of 2.40 Å in the gaseous state (Braune & Knoke, 1933).

The observed geometry for bromomercurates is roughly given as tetrahedral (Fig. 4), octahedral (Fig. 5) and trigonal bipyramidal (Fig. 6). The averaged

longer distances ( $r_L$ ) are plotted *versus* the averaged shorter distances ( $r_S$ ). The observed values are fitted by the function  $r_L = d + 1/[e(d - r_S)]$  where  $e$  is a fitting value.

It is clear from Figs. 4, 5 and 6 that no distances shorter than 2.4 Å, the distance in gaseous  $\text{HgBr}_2$ , are observed. Some experimental values however, approach this value. The upper limit of  $\text{Hg}-\text{Br}$  distances is given by a regular polyhedron with bonds of equal length. These distances in regular polyhedra are indicated by an angle bisector in the correlation diagram. Only in the case of tetrahedral coordination, are values close to the regular ideal ones observed. For coordinations described as approximately octahedral and trigonal bipyramidal a pronounced distortion is found. The constant  $e$  in the fitting function has a value of  $e = -27.7$  (tetrahedral),  $-18.11$  (octahedral) and  $-13.22 \text{ \AA}^{-2}$  for the trigonal bipyramid.

The present survey demonstrates the great variety of  $\text{Hg}$  coordinations in bromomercurates which makes a classification in terms of regular polyhedra meaningless.

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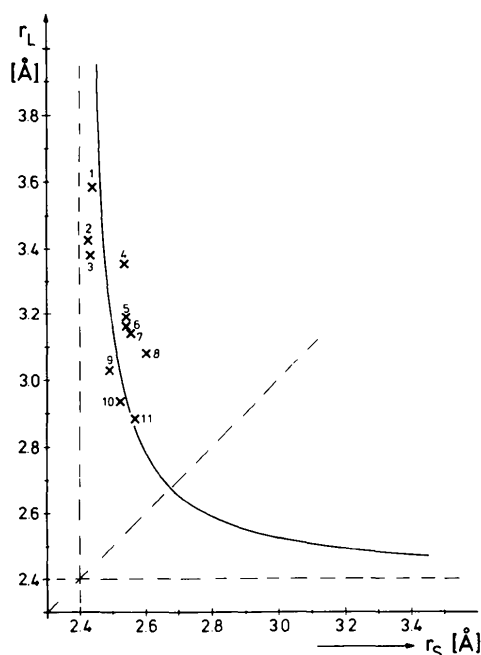


Fig. 6. Correlation diagram for bipyramidal  $\text{HgBr}$  coordinations. References: 1,  $\text{C}_9\text{H}_{15}\text{O}_2\text{HgBr}$  (Porter, Cud, Miller & McPhail, 1980); 2,  $\text{CH}_3\text{CN}\cdot 3\text{HgBr}_2$  (Leligny *et al.*, 1972); 3,  $\text{Fe}(\text{CO})_4(\text{HgBr})_2$  (Baird & Dahl, 1967); 4,  $[(\text{CH}_3)_3\text{NH}]\text{HgBr}_3$  (this paper); 5,  $[\text{CH}_3\text{NH}_3]\text{HgBr}_3$  (Körfer *et al.*, 1985); 6,  $\text{CsHg}_2\text{Br}_5$  (Pakhomov, Fedorov & Ivanova-Korfini, 1979); 7,  $(\text{C}_{10}\text{H}_8\text{N}_2\cdot\text{HgBr}_2)_2$  (Craig, Farhangi, Graddon & Stephenson, 1973); 8,  $\text{Hg}_2\text{NHBr}_2$  (Brodersen, 1955); 9,  $(\text{C}_7\text{H}_9\text{N})\text{HgBr}_2$  (Bell, Goldstein, Jones & Nowell, 1980); 10,  $[(\text{CH}_3)_4\text{N}]\text{HgBr}_3$  (White, 1963); 11,  $\text{C}_8\text{H}_{16}\text{N}_2\text{O}_2\text{S}_2\text{HgBr}_4$  (Book, Carty & Chieh, 1981).

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## Structures of Bis(4-aminopyridinium) Tetrachlorocuprate(II) Monohydrate, $[\text{C}_5\text{H}_7\text{N}_2]_2[\text{CuCl}_4] \cdot \text{H}_2\text{O}$ , and Bis(2-amino-3-hydroxypyridinium) Tetrachlorocuprate(II), $[\text{C}_5\text{H}_7\text{N}_2\text{O}]_2[\text{CuCl}_4]$ : Correlation of $\text{CuCl}_4^{2-}$ Geometry with Hydrogen Bonding and Electronic Structure

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### Abstract

$[\text{C}_5\text{H}_7\text{N}_2]_2[\text{CuCl}_4] \cdot \text{H}_2\text{O}$ ,  $M_r = 413.62$ , monoclinic,  $C2/c$ ,  $a = 8.457(2)$ ,  $b = 14.318(2)$ ,  $c = 14.382(2)$  Å,  $\beta = 95.82(1)^\circ$ ,  $V = 1732.4(5)$  Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.59$  g cm<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.71069$  Å,  $\mu = 18.79$  cm<sup>-1</sup>,  $F(000) = 836$ ,  $T = 293$  K. The 1526 unique reflections ( $2\theta \leq 50^\circ$ ), of which 1288 had  $F_o \geq 3\sigma(F_o)$ , refined to a final  $R$  of 0.035 and  $wR = 0.038$ .  $[\text{C}_5\text{H}_7\text{N}_2\text{O}]_2[\text{CuCl}_4]$ ,  $M_r = 427.6$ , triclinic,  $P\bar{1}$ ,  $a = 7.554(1)$ ,  $b = 7.968(2)$ ,  $c = 14.578(3)$  Å,  $\alpha = 103.23(2)$ ,  $\beta = 93.30(2)$ ,  $\gamma = 99.59(2)^\circ$ ,  $V = 838.0(3)$  Å<sup>3</sup>,  $Z = 2$ ,  $D_x = 1.69$  g cm<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.71069$  Å,  $\mu = 19.6$  cm<sup>-1</sup>,  $F(000) = 430$ ,  $T = 293$  K. The 2185 unique reflections ( $2\theta \leq 45^\circ$ ), of which 1680 had  $F_o \geq 3\sigma(F_o)$ , refined to a final  $R$  of 0.047 and  $wR = 0.040$ . The structures of both compounds consist of discrete  $\text{CuCl}_4^{2-}$  anions and organic cations with the stoichiometric formulas indicated in the title. The geometry of both of the  $\text{CuCl}_4^{2-}$  ions is intermediate between tetrahedral and square planar,

with *trans* angles (average) of 134.6 and 137.8° respectively, and Cu—Cl distances (average) of 2.247 Å for both salts. The structural chemistry of 62 isolated  $\text{CuCl}_4^{2-}$  anions is reviewed. The *trans* Cl—Cu—Cl angles in non-disordered  $\text{CuCl}_4^{2-}$  anions range from 125 to 180°. Correlations of this *trans* Cl—Cu—Cl angle with hydrogen bonding to the cation, with the average Cu—Cl distance, and with the *d-d* electronic transition energy are examined. Finally, a review is given of structures in which the  $\text{CuCl}_4^{2-}$  anion acts as a coordinating ligand.

### Introduction

A major goal of the research program in this laboratory has been the synthesis and characterization of various copper(II) halide oligomers. A particularly fruitful approach has employed substituted pyridinium cations as counterions. In the process of these syntheses, the 4-aminopyridinium (4AP) and 2-