

# The Crystal Structure of Tetramethylammonium Hexabromotellurate(IV)

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The room temperature crystal structure of  $[(\text{CH}_3)_4\text{N}]_2[\text{TeBr}_6]$  has been investigated by means of single crystal X-ray diffraction. The compound crystallizes in the cubic space group  $Fd\bar{3}c$  ( $O_h^8$ , No. 228), with  $a=26.563(3)$  Å and  $Z=32$ . The intensities of 220 independent reflections with  $I > 3\sigma(I)$ , collected with an automatic diffractometer, were used to refine the structural parameters for all non-hydrogen atoms by least-squares techniques to an  $R$  of 0.036. The structure found clearly deviates from previous results on analogous tetramethylammonium hexahalometallates. These compounds were reported to crystallize in the antiferroite space group  $Fm\bar{3}m$  ( $O_h^5$ , No. 225), with  $Z=4$  ( $\text{K}_2\text{PtCl}_6$  type). Probably this is correct only to a first approximation.

Tetramethylammonium-containing crystals of general formula  $((\text{CH}_3)_4\text{N})_2[\text{MX}_6]$ , where  $M$  is a quadrivalent metal and  $X$  is a halogen, are known to undergo phase transitions at lower temperatures. In this context spectroscopic and structural properties of these compounds have been examined.<sup>1–3</sup> The crystalline compounds have hitherto been described by an antiferroite lattice of  $\text{K}_2\text{PtCl}_6$  type (space group  $O_h^5$ ,  $Fm\bar{3}m$ ,  $Z=4$ ) and a “perpendicular” arrangement<sup>3</sup> of methyl groups, although some minor deviations from the  $O_h^5$ -symmetry could not be explained.<sup>2,3</sup>

In tetramethylammonium hexabromotellurate  $[(\text{CH}_3)_4\text{N}]_2[\text{TeBr}_6]$  the X-ray powder pattern<sup>4</sup> showed a more pronounced deviation from the  $O_h^5$  symmetry and this compound was therefore selected for detailed investigation.

## EXPERIMENTAL

Tetramethylammonium hexabromotellurate(IV) was prepared by dissolving  $\text{TeO}_2$  in hot ( $\sim 80^\circ\text{C}$ ) concentrated hydrobromic acid and adding an equivalent amount of  $(\text{CH}_3)_4\text{NBr}$  dissolved in a minimum of water. The orange red precipitate was separated, washed with ethanol and recrystallized from hot concentrated acid. Analysis: Br found: 64.3%; Br calc.: 63.4%. Crystals of octahedral shape and of a size suitable for X-ray work were obtained during slow cooling (1 h). Lattice type and space group were determined from Weissenberg photographs using Cu radiation. A crystal with an edge size of ca. 0.1 mm was used for intensity data collection on an automatic four circle diffractometer (CAD4-F), using graphite monochromatized  $\text{MoK}\alpha$  radiation. The 2979 reflections collected with  $\theta < 25^\circ$  were corrected for Lorentz and polarization effects. Absorption correction was carried out by the empirical method described by Flack.<sup>5</sup> Averaging over symmetry-related reflections gave 885 unique reflections of which 220 with  $I > 3\sigma(I)$ , were considered as observed. The internal consistency indices  $R_i = \sum |F_o|^2 - \langle F_o^2 \rangle / \sum F_o^2$  for the observed reflections before and after correction for absorption were 0.042 and 0.030, respectively. The calculations included a correction for anomalous dispersion of Te and Br<sup>6</sup> and full-matrix least-squares refinements<sup>7</sup> of positional and thermal parameters. The obtained final  $R$ -values were  $R = \sum |F_o - F_c| / \sum |F_o| = 0.036$  and  $R_w = (\sum w(|F_o| - |F_c|)^2 / \sum w F_o^2)^{1/2} = 0.046$ ; with weights  $w$  proportional to  $\min(\sin \theta / a\lambda, a\lambda / \sin \theta) \min(F/b, b/F)$ . The constants  $a$  and  $b$  were determined<sup>8</sup> to 0.3791 and 387.16, respectively. No pronounced peak was seen in the final difference electron density map.

A list of observed and calculated structure factors can be obtained from the authors on request.

*Crystal Data.*  $((\text{CH}_3)_4\text{N})_2\text{TeBr}_6$ .  $M = 754.35$  g/mol. Cubic. Space Group  $Fd\bar{3}c$  ( $O_h^8$ , No. 228).  $a = b = c = 26.563(3)$  Å at 22 °C.  $V = 18742.6$  Å<sup>3</sup>.  $Z = 32$ .  $D_c = 2.14$ ;  $D_o = 2.16$  g/cm<sup>3</sup>.  $\mu(\text{MoK}\alpha) = 121.5$  cm<sup>-1</sup>. Reflection conditions,  $hkl$ :  $h + k, k + l = 2n$ ;  $hhl$ :  $l = 2n$ ;  $0kl$ :  $k + l = 4n$  and cyclic permutations. The unit cell dimension was determined from optimum single crystal diffractometer settings.

## RESULTS AND DISCUSSION

The final structural parameters are given in Table 1. The bond lengths and bond angles are

listed in Table 2 and are very close to commonly accepted values; the shorter C–N distance (1.48 Å) of the  $(\text{CH}_3)_4\text{N}$  ion formed from the C1 and N1 atoms is probably due to larger libration of this ion.

The only previous structural knowledge on the compound seems to be the observation by Nakamura *et al.*<sup>4</sup> that it has a *single* <sup>79</sup>Br pure quadrupole resonance line at room, dry ice and liquid nitrogen temperatures, “although the observed X-ray powder pattern indicated a crystal structure quite different from that of potassium hexachloroplatinate(IV)”.<sup>4</sup> Both observations are in accordance with what is deduced from our results: All bromide

*Table 1.* Positional and thermal parameters ( $U_{ij}$  in units of  $10^{-4}$  Å<sup>2</sup>) with estimated standard deviations for independent ones. The temperature factor expression is  $\exp[-(2\pi^2 \sum_{ij} h_i h_j a_i^* a_j^* U_{ij})]$  or  $\exp[-8\pi^2(\sin \theta/\lambda)^2 U^2]$ .

Atom	Site symmetry	$x/a$	$y/b$	$z/c$	$U_{11}$ or $U$	$U_{22}$	$U_{33}$	$U_{12}$	$U_{13}$	$U_{23}$
Te	$\bar{3}$	0.0	0.0	0.0	521(7)	521	521	-4(12)	-4	-4
Br	1	0.1008(1)	0.0090(1)	-0.0095(1)	549(11)	751(21)	849(22)	-28(10)	1(10)	105(10)
N1	$\bar{2}$	0.125	0.125	0.125	494(230)					
N2	$\bar{4}$	0.375	0.125	0.125	533(91)					
C1	3	0.157(2)	0.157	0.157	1820(318)					
C2	1	0.115(1)	0.171(1)	0.407(1)	757(66)					

*Table 2.* Interatomic distances (Å) and angles (°) of the  $((\text{CH}_3)_4\text{N})_2[\text{TeBr}_6]$  structure, compared with values on related structures.

	This work	Literature
Te–Br	2.701(2)	$\sim 2.70(1)^a$
Te–C1	> 5.1	(5.2) <sup>b</sup>
Te–C2	4.83(2)	(5.2) <sup>b</sup>
Br–Br	3.794(3), 3.845(3)	$\sim 3.80^a$
Br–C1	3.82(2), 4.788(4), 4.962(4)	
Br–C2	3.69(2), 4.03(2), 4.06(2), 4.06(2), 4.08(2), 4.36(2)	
Br–N1	4.762(3)	
Br–N2	4.395(3), 4.742(3), 5.084(3)	
C1–N1	1.48(4)	1.484(6) <sup>b</sup>
C2–N2	1.52(2)	1.484(6) <sup>b</sup>
C1–C1	2.42(6)	2.42(1) <sup>b</sup>
C1–C2	4.97(2)	4.65(2) <sup>b</sup>
C2–C2	2.47(3), 2.50(3), 4.28(3)	2.42(1), 4.65(2) <sup>b</sup>
Br–Te–Br	89.2(1), 90.8(1), 180	$\sim 90^\circ \pm 0.3^a$
C1–N1–C1	109(1)	109.47
C2–N2–C2	109(1), 111(1)	109.47

<sup>a</sup> For  $\text{K}_2[\text{TeCl}_6]$ ,  $(\text{NH}_4)_2[\text{TeBr}_6]$  and  $\text{Cs}_2[\text{TeBr}_6]$ , see Brown<sup>9</sup> and Das and Brown.<sup>10</sup> <sup>b</sup> For Pt–Cl structure, see Ref. 2.

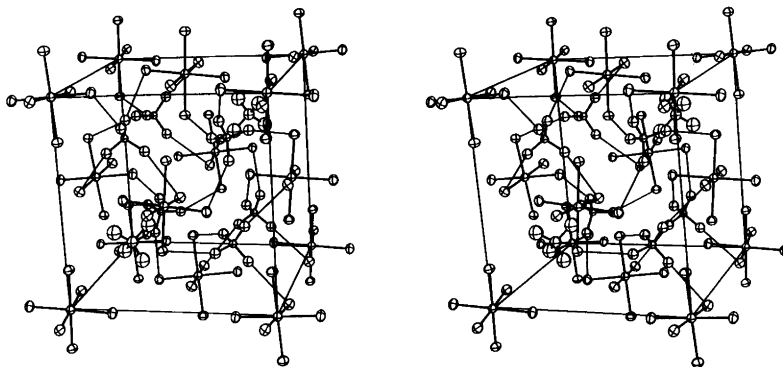


Fig. 1. Stereoscopic view<sup>12</sup> of the structure of tetramethylammonium hexabromotellurate(IV). Only one eighth of the cell is shown. Thermal ellipsoids depict 30% of the charge density. The short C2–Br contacts are shown.

atoms are identical, yet the structure is different from the antifluorite structure  $Fm\bar{3}m$  characterizing most  $A_2MX_6$  crystals.<sup>11</sup>

For the purpose of comparison, a fraction of the  $[(\text{CH}_3)_4\text{N}]_2[\text{TeBr}_6]$  unit cell is illustrated in Fig. 1, in the same way as previously<sup>2</sup> for the  $((\text{CH}_3)_4\text{N})_2[\text{PtCl}_6]$ . The results of the comparison of the two structures are:

(i) There is a doubling of the repeat unit in the  $Fd\bar{3}c$  structure (Te salt), relative to the  $Fm\bar{3}m$  structure, resulting in an 8 fold increase in  $Z$ . One manifestation of this is that the  $[\text{TeBr}_6]^{2-}$  ions depicted in Fig. 1 are not all related by mere translation.

(ii) There is a decrease in the symmetry of the  $[\text{TeBr}_6]^{2-}$  ions to  $\bar{3}\equiv S_6$ ; i.e., the coordination of bromine around tellurium is not perfectly octahedral, as in an  $Fm\bar{3}m$  structure. The six Br atoms form a slightly flattened trigonal antiprism (Br–Te–Br angles being 89.2 and 90.8°). The antiprism has two larger (equilateral) and six smaller triangular faces.

(iii) The Te–Br bonds form an angle of 7.4° with the cubic translation axes. The deviation (of the  $[\text{TeBr}_6]^{2-}$  ions) from the  $Fm\bar{3}m$  structure consists predominantly of rotations of  $[\text{TeBr}_6]^{2-}$  ions around  $\bar{3}\equiv S_6$  symmetry axes. These axes point towards the more librating  $(\text{CH}_3)_4\text{N}^+$  ion. The rotations amount to 9.1° around  $\{111\}$ -type vectors.

(iv) In the  $Fm\bar{3}m$  structure, the tetramethylammonium ions are all identical and of  $43m\equiv T_d$  symmetry; in  $Fd\bar{3}c$  they are divided in two sets:

One set of  $23\equiv T$  symmetry (16 ions) and another set of  $\bar{4}\equiv S_4$  symmetry (48 ions). The 64 C1 methyl groups in set 1 have a local  $3\equiv C_3$  symmetry, whereas the 192 C2 methyl groups in set 2 have no local symmetry (other than  $1\equiv C_1$ ). Tetramethylammonium ions of set 1 approach the larger of the  $[\text{TeBr}_6]^{2-}$  faces and *vice versa*; and similarly for set 2 and the smaller faces.

To summarize, it is seen that the  $Fm\bar{3}m$  and  $Fd\bar{3}c$  models differ in such a way that if the perturbations described above for  $((\text{CH}_3)_4\text{N})_2[\text{TeBr}_6]$  approach zero, then the two descriptions become equivalent. In the  $Fm\bar{3}m$  structure each halogen has four methyl nearest neighbours and each methyl group has three equal contacts with halogen. In the  $Fd\bar{3}c$  structure of  $((\text{CH}_3)_4\text{N})_2[\text{TeBr}_6]$ , perturbations occur so that shorter and longer methyl–bromide contacts are formed. The short contact distance (3.69 Å) is found between one C2 and one Br, both placed in general positions. The short contact distance, which is indicated in Fig. 1, is significantly shorter than the standard van der Waals contact distance between *neutral* methyl and bromine groups (3.95 Å).<sup>13</sup> The longer contact distances (3.82 Å) are found between the remaining methyl groups (C1) and bromine. Apparently, an  $Fd\bar{3}c$  structure in which some of the methyl groups (C2) approach one particular bromine quite closely is more favourable than an  $Fm\bar{3}m$  structure where all methyl–bromine contacts are equivalent. Since there are too many methyl groups relative to the number of available bromine atoms, some of the tetramethylammonium ions (set 1) attain space

for larger librations. Presumably, the short C2 methyl-bromine contacts are caused by mutual attraction due to fractional charges. Weak  $\text{CH}_3-X$  interactions ( $X = \text{Cl}, \text{Br}$ ) have been observed in low temperature Raman spectra<sup>1,14</sup> and in this respect the charged methyl groups of the tetramethylammonium ion differ from the average methyl group in the organic chemistry.

The same features, but less pronounced, are supposed to occur in, e.g., the  $[(\text{CH}_3)_4\text{N}]_2[\text{PtCl}_6]$  salt.<sup>2</sup> We have reexamined the second data set of Ref. 2 from this point of view. The use of space group  $Fd3c$  indeed allowed us to reproduce the weak  $Fm3m$ -forbidden reflections to an  $R$  value of the order 0.05 (only including these forbidden reflections). This result should be considered as tentative, since the data set only contained the even  $hkl$  reflections corresponding to an  $Fd3c$  structure of  $[(\text{CH}_3)_4\text{N}][\text{PtCl}_6]$ .

The crystal structure of  $((\text{CH}_3)_4\text{N})_2[\text{SnCl}_6]$  has recently been solved<sup>15</sup> to  $R = 0.066$  (910 reflections), using the  $Fm3m$  space group. The positional and thermal parameters were essentially equivalent to the Pt results.<sup>2</sup> The authors suggested that the high  $R$ -value and the thermal parameters for C and Cl could be due to "some disorder in the crystal, particularly in the position of the  $[(\text{CH}_3)_4\text{N}]^+$  ions".<sup>15</sup> In view of the present investigation, the phenomenon observed is possibly not disorder but order in space group  $Fd3c$ . It would be interesting to examine this and other  $((\text{CH}_3)_4\text{N})_2[\text{MX}_6]$  crystal structures from this point of view.

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