A Possible Triaquohydrogen Ion H_7O_3 : Crystal Stucture of 1,1′-Tetramethylene-2,2′-bipyridylium Dibromide.$H_2O.\frac{1}{3}HBr$

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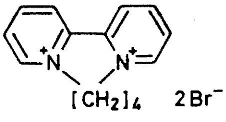
Summary *X*-Ray crystallographic analysis indicates that crystals of the title compound contain the triaquohydrogen ion $H_7O_3^+$.

THE effect of the magnitude of the dihedral angle between the planes of the pyridinium rings on the length of the central C(sp^2)–C(sp^2) bond in diquaternary salts of 2,2′-bipyridyl is of interest in connection with studies of the relationship between structure and the herbicidal activity exhibited by certain of these salts.[1,2]

Our present analysis shows that in the inactive salt 1,1′-tetramethylene-2,2′-bipyridylium dibromide (I) the inter-ring angle is 65·8° and the length of the central bond is 1·48Å, in good agreement with accepted values for the C(sp^2)–C(sp^2) single bond length.[3]

Crystals of (I) belong to space group $R\bar{3}c$ (D_{3d}^6) with

18 units of $(C_{14}H_{16}N_2)^{2+}2Br^{-}.H_2O.\frac{1}{3}HBr$ in the hexagonal cell, $a = 18{\cdot}48$, $c = 24{\cdot}84$Å. The organic cation has crystallographic symmetry $2(C_2)$. The *X*-ray intensity data were recorded on equi-inclination Weissenberg photographs using Cu–K_α radiation and measured photometrically. The structure was solved by the heavy-atom technique, and positional and anisotropic thermal parameters refined by least-squares. The hydrogen atoms of the organic cation were included in the calculations with fixed co-ordinates. The final value of R is 7·4% for 1227 observed structure amplitudes.



(I)

Bond lengths and angles for the cation (I), which have estimated standard deviations of about 0·015Å and 0·7°, respectively, agree well with generally accepted values and will be discussed elsewhere. Of particular interest, however, is the nature of the water and hydrogen bromide of crystallisation.

There is no evidence for the occurrence of HBr molecules. If HBr were present in the crystal, one might expect Br–H $\cdots$ Br^- hydrogen bonding.[4] However, this does not occur here. Of the 42 bromide ions in the unit cell, 36 occupy general positions and 6 are at the special positions $(0,0,\frac{1}{4})$, $(0,0,\frac{3}{4})$ *etc.*, with all Br $\cdots$ Br contact distances >4Å. Related to this, is the nature of the water.

A Fourier difference synthesis calculated on the basis of the whole structure except the molecule of water and the hydrogen of the HBr, showed no significant features apart from two sets of peaks in general positions grouped fairly close to the six-fold positions (0,0,0), $(0,0,\frac{1}{2})$ *etc.*, point symmetry $\bar{3}(S_6)$. The peaks of one set are of about 1/3 the expected height of an oxygen peak, while those of the second set, situated closer to the $\bar{3}$ sites are of about half the height of the first set. The required number of 18 water molecules per unit cell is obtained, in a manner consistent with the observed Fourier peak heights, by assuming that one-third of the sites of the first set of peaks and one-sixth of those of the second set are occupied by oxygen atoms. If, as seems reasonable, there are precisely three water molecules in the vicinity of each $\bar{3}$ site (statistically, the requirement is only that the *average* number at each $\bar{3}$ site should be three), then, excluding arrangements involving O $\cdots$ O distances of less than 2Å, only two distinct configurations for the water molecules are possible. These are illustrated in the Figure. The positioning of the hydrogen atoms is purely schematic.

The O $\cdots$ O distances of 2·40 and 2·46Å (both ±0·06Å) are considerably shorter than hydrogen bonds between normal water molecules, but agree well with those found for the very short hydrogen bonds in aquohydrogen ions where two or three water molecules are associated with a *proton*.[5–10] It is clear, therefore, that the proton of the HBr has been transferred to water, so that the structures illustrated in the Figure may be formulated as (a) $H_7O_3^+$ and (b) $H_5O_2^+.H_2O$. The O $\cdots$ Br^- distances of 3·17, 3·21, and 3·29Å are within the range of values found for O–H $\cdots$ Br^- hydrogen bond distances in other, comparable structures.[9]

The i.r. spectrum is also consistent with this picture of strong, possibly symmetric, O $\cdots$ H $\cdots$ O hydrogen bonding. It shows a broad absorption extending over the region 900—1700 cm^{-1}, a feature found in a number of systems, such as the type *A* acid salts,[11] in which symmetric or near symmetric hydrogen bonding is known to occur.

It does not seem possible to distinguish between the two configurations $H_7O_3^+$ and $H_5O_2^+.H_2O$ [Figure (a) and (b)] from the *X*-ray or spectroscopic data alone, and because of the statistical distribution of these species about the $\bar{3}$ sites, it is unlikely that neutron diffraction data would yield unambiguous results. However, comparison with the results obtained on crystals of the various hydrates of strong acids containing aquohydrogen ions,[5–10] supports the first alternative, the $H_7O_3^+$ configuration, with all the available hydrogen atoms participating in the formation of strong hydrogen bonds. In (b), the interaction between the $H_5O_2^+$ ion and the water molecule would involve, at best, only extremely weak hydrogen bonding. The configuration $H_5O_2^+.H_2O$ occurs in the crystal structure of $HCl.3H_2O$,[6] but here the $H_5O_2^+$ ions form good hydrogen bonds to the water molecules in a chain structure, with $d(H_5O_2^+ \cdots H_2O) = 2{\cdot}65$ and 2·75Å. On the other hand, the structure and environment of the $H_7O_3^+$ configuration [Figure (a)] is similar to that found in the two previously reported examples of its occurrence.[9,10] We therefore formulate the crystal structure of the title compound as $18(C_{14}H_{16}N_2)^{2+}.42Br^{-}.6H_7O_3^{+}$.

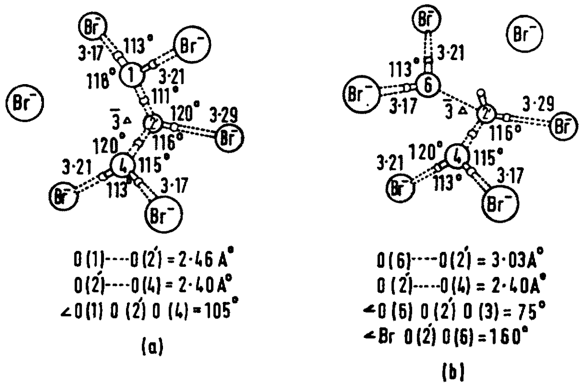


FIGURE. *The two possible configurations for the water of hydration as viewed down the* c-*axis.* (*a*) $H_7O_3^+$, (*b*) $H_5O_2^+.H_2O$. *A second variant of* (*b*) *has very similar dimensions, with* d (O . . . O) = 2·46 and 3·06Å, $\angle$O . . . O . . . O = 74°. *The labelling of the oxygen atoms is derived from a numbering scheme in which the two sets of six oxygen peaks around the* $\bar{3}$ *site* (*see text*) *are numbered* 1–6 *and* 1′–6′ *respectively, in a clockwise direction.*

Beecham *et al.*,[12] have proposed that the diaquohydrogen ion, $H_5O_2^+$, is a stable entity in aqueous solutions of acids. In view of the more recent results on crystals containing the triaquohydrogen ion, $H_7O_3^+$, it would seem possible that it also might exist as a stable entity in solution.

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