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A Crystalline $[H_9O_4]^+$ Hydronium Ion Salt with a Weakly Coordinating Anion

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Brønsted acids with weakly coordinating anions, for example[1] $[H(OEt_2)_2]^+[BAr^F{}_4]^-$, methane-based acids,[2] and ammonium salts,[3] are very useful reagents for generating cationic organotransition metal complexes and catalysts.[1-4] In this paper, we introduce a well-defined Brønsted acid salt of the $H_9O_4^+$ hydronium ion having an exceptionally robust, weakly-coordinating counterion, the *closo*-carborane $CB_{11}H_6Br_6^-$. Weighable strong acids that are crystalline at room temperature and which have precisely determined numbers of water molecules may prove to be generally useful as reagents. A further interesting feature of this new reagent is its X-ray structure. $[H_9O_4]^+[CB_{11}H_6Br_6]^-$ is a rare example of a hydronium ion salt with discrete $H_9O_4^+$ ions. The structure is very close to that proposed 40 years ago by Eigen on the basis of mobility studies for the hydronium ion in liquid water.[5,6]

We first came upon crystalline $[H_9O_4]^+[CB_{11}H_6Br_6]^-$ while investigating the nature of the hydrolysis products of silylium ion-like species such as $(R_3Si^{\delta+})(CB_{11}H_6Br_6{}^{\delta-})$. With minimal water, the strong Lewis acidity of the silylium ion is translated into Brønsted acidity, and a protonated silanol is produced (eq 1).[7] With further H_2O, the greater basicity of water (versus

$$R_3Si(CB_{11}H_6Br_6) + H_2O \rightarrow [R_3Si(OH_2)]^+[CB_{11}H_6Br_6]^- \qquad (1)$$

silanol) naturally leads to hydronium ion formation (eq 2). Single

$$[R_3Si(OH_2)]^+[CB_{11}H_6Br_6]^- + 4H_2O \rightarrow [H_9O_4]^+[CB_{11}H_6Br_6]^- + R_3SiOH \qquad (2)$$

crystals suitable for X-ray diffraction were obtained from dichlorobenzene solution by vapor diffusion with *n*-hexanes.[8]

As shown in Figure 1, the crystal structure consists of discrete $H_9O_4^+$ and $CB_{11}H_6Br_6^-$ ions. The nearest O···O approach between cations is 4.58 Å, too long for H-bonding. A perspective view of the cation is shown in Figure 2, and key dimensions are given in Table 1. The idealized formulation is of an sp^3 hybridized H_3O^+ ion hydrated by three water molecules with linear O–H···O hydrogen bonding.

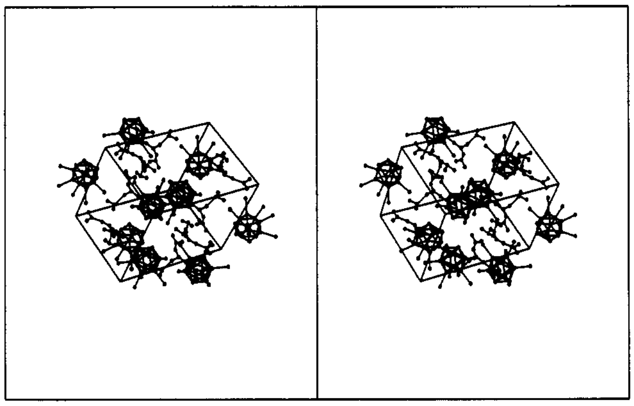

Figure 1. Stereoscopic unit cell packing diagram of $[H_9O_4][CB_{11}H_6Br_6]$ showing discrete ions.

Table 1. Dimensions of the $H_9O_4^+$ Cation

distance (Å)		angle (deg)	
O1···O2	2.505(21)	O2–O1–O3	103.4(8)
O1···O3	2.506(23)	O2–O1–O4	117.0(8)
O1···O4	2.532(22)	O3–O1–O4	104.0(8)

An Eigen-type structure for the $H_9O_4^+$ ion, having a central H_3O^+ moiety pyramidally surrounded by three water molecules, was first observed in the solid state two decades ago by Almlöf, Lundgren, and Olovsson in the X-ray crystal structures of low-temperature hydrates of HBr and $HClO_4$.[9a] Although these hydronium salts did not contain discrete cations, $H_9O_4^+$ ions (as well as related $H_5O_2^+$ and $H_7O_3^+$ ions) were discernible entities within the H-bonded arrays. There is a structural parallel in $[H_3O]^+[AsF_6]^-$, where strong H-bonding to fluorine stabilizes the pyramidal H_3O^+ ion.[9b] To our knowledge, the only structurally characterized hydronium salt with discrete $H_9O_4^+$ ions is found in the much more recent work of Krebs *et al.*[10] with hydrates of bromotellurous acid. Crystals of $[H_9O_4]^+[Te_3Br_{13}]^-$ were isolated and studied at subambient temperatures. The gross structure of the $H_9O_4^+$ ion was found to be of the Eigen type with some flattening of the pyramidal structure of oxygen atoms from the sp^3 ideal (average O···O···O = 117.1(9)°).[10] By contrast, the present structure has an average O···O···O angle of the 108.1(8)°, although one of the angles is 117.0(8)° (see Table 1). There is a range of ~15° in these angles in the reported solid state structures containing the $H_9O_4^+$ ion, and this probably reflects the degree of distortion that can be propagated by packing influences and H-bonding. "Gas phase" *ab initio* calculations have been reported that place the pyramidalization angle at 117.3° and at 115.3°.[11,12] C_{3v} symmetry is imposed on these calculations, and the water molecules

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(8) Crystal data: monoclinic, $P2_1/n$, $a = 10.480(3)$ Å, $b = 11.994(5)$ Å, $c = 15.785(4)$ Å, $\beta = 90.05(2)°$, $V = 1984.1(13)$ Å^3 for $Z = 4$; $R = 0.0501$ for 1522 observed reflections with $F > 4.0\sigma(F)$; data at 153 K. The structure was solved by direct methods, the H atoms being located by the low-angle scattering method (Kirtley, S. W.; Olsen, J. P.; Bau, R. *J. Am. Chem. Soc.* **1973**, *95*, 4532–4536), and refined by full-matrix least-squares methods.

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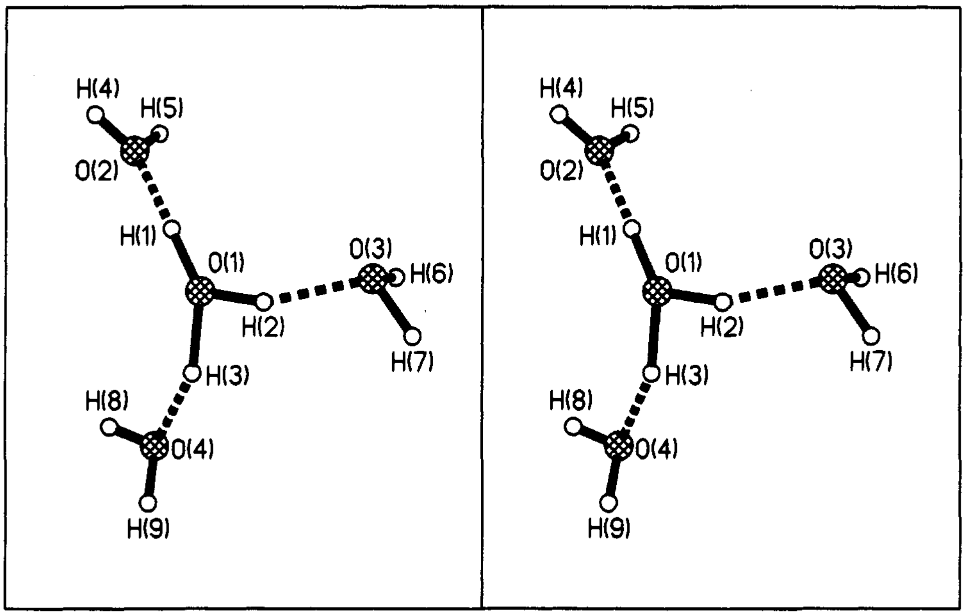

Figure 2. Perspective view (in stereo) of the $H_9O_4^+$ cation.

are "perpendicular" rather than "flat"; i.e. the dihedral angles made by the water molecules and the trigonal plane of the three basal O atoms are 90°. These angles are 75.5, 71.7, and 53.0° in the present structure, but because the H atoms are not well located in most structures, it is presently difficult to experimentally assess any connection that might exist between these dihedral angles and H_3O^+ pyramidalization angles. The same comment applies to the question of whether the O−H···O bonds are linear. Neutron diffraction studies on the related $H_5O_2^+$ ion support linearity.[13]

The three O···O distances between the central H_3O^+ ion and its three solvating water molecules in the present structure (2.50(2)−2.53(2) Å) are nearly equivalent. They are near the short end of the range observed for other $H_9O_4^+$ structures (2.45−2.60 Å),[10] shorter than the average (2.56 Å), and close to the *ab initio* calculated values (2.53−2.57 Å).[11,12] This probably reflects the discrete and essentially isolated nature of the $H_9O_4^+$ ions and their relatively weak electrostatic interaction with specific atoms of the large, diffusely-charged carborane anion. Nevertheless, the array of closest cation/anion O···Br distances (3.45−3.80 Å) should probably be viewed in terms of weak, if rather directionless, H-bonding between cations and anions. Only one of these O−H···Br interactions seems to cause much perturbation of the structure of the cation. The shortest O···Br approach is O4···Br9 and is probably the cause of the slight lengthening of the O1···O4 distance relative to the other two O···O distances. The hydrogen atoms were all located and refined isotropically, but neutron diffraction data will be necessary before a more detailed analysis of H-bonding can be made. What can be said at this time is that the data are consistent with essentially linear O−H···O bonding around the central H_3O^+ ion. In the most recent *ab initio* calculation,[12] an angle of 176.9° is reported.

As a reagent, $[H_9O_4][CB_{11}H_6Br_6]$ is readily prepared in synthetic quantities by treatment of $Ag(CB_{11}H_6Br_6)$ with 1 equiv of 6 M aqueous hydrochloric acid, filtration to remove the AgCl precipitate, and evaporation to dryness under vacuum. Recrystallization from *m*-dichlorobenzene gives colorless crystals in 85% yield. The reagent has been characterized by satisfactory elemental analysis (C, H, Br) and differential thermal analysis. At ca. 140 °C, it undergoes a 4.9% weight loss corresponding to the loss of two water molecules (theoretical 5.2%), perhaps forming the known[9a,13] $H_5O_2^+$ ion. The crystalline reagent is somewhat hygroscopic and is best stored in a drybox. As an example of its use as a protonation reagent, we have used it to protonate the (μ-oxo)diiron(III) tetraphenylporphyrin dimer (TPP)Fe−O−Fe(TPP). The product is the (μ-hydroxo)diiron(III) cation $[(TPP)Fe-O(H)-Fe(TPP)]^+$ which is formed in quantitative yield by NMR. Its unusual structure and properties are the subject of a separate publication.[14] The importance of controlled minimal water content in this reaction is reflected in the observation that excess aqueous acid leads to cleavage of the dimer and formation of the diaquo cation $[Fe(H_2O)_2(TPP)]^+$.[15] The importance of a very weakly coordinating anion to the success of this dimer protonation reaction is illustrated by the observation that acids with more strongly coordinating anions, such as triflic acid, lead to products with a coordinated anion, e.g. $Fe(OSO_2CF_3)(TPP)$.[16]

In summary, by using a large inert counterion, it is possible to prepare discrete hydronium ion salts that are stable crystalline reagents at room temperature, have precisely defined hydration content, and are uniquely suited for certain demanding protonation reactions. Future work will explore the possibility of isolating stronger acids with fewer stabilizing solvent molecules.

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Supporting Information Available: An atom-numbering diagram and tables of fractional atomic coordinates, thermal parameters, interatomic bond distances and angles, and text giving the details of X-ray crystal analysis (10 pages). This material is contained in many libraries on microfiche, immediately follows this paper in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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