Synthesis and Structure of Solvated Protons Incorporating Weakly Coordinating Anions. Precursors of Superacids†

TSANG, Chi-Wing(曾志荣) YANG, Qing-Chuan(杨清传) MAK, Thomas C. W.(麦松威)
XIE, Zuo-Wei*(谢作伟)
Department of Chemistry, The Chinese University of Hong Kong, Shatin, New Territories, Hong Kong, China

Six new solvated proton salts of highly halogenated carborane anions, [H(solvent)$_n$][carborane] (carborane = 1-R-$CB_{11}Y_5X_6^-$ (R = H, Me; X, Y = Cl, Br, I), 1-H-$CB_9Br_9^-$) were prepared from the salt metathesis reaction of Ag(carborane) and HCl in high yields. Single-crystal X-ray analyses show that they are all discrete molecules in the solid-state. The number of the solvated molecules surrounding H^+ ion can not be determined with the knowledge of the size and substituents of the carborane anions. These salts provide convenient weighable sources of Brønsted acid reagents having a wide range of acidities and good thermal stabilities. TGA results indicate that the solvated molecules (water or organic molecules) in the cations [H(solvent)$_n$]$^+$ can be removed under high temperature and high vacuum conditions to give superacidic materials H(carborane) which can protonate olefin.

Keywords carborane, solvated proton, hydronium ion, superacid, hydrogen bonding

Introduction

It is universally understood that writing H^+ is shorthand for a solvated proton, [H(solvent)$_n$]$^+$, the value of n and the details of the coordination environment are often unspecified. Isolation and structural characterization of various salts containing representative [H(solvent)$_n$]$^+$ cations will certainly lead to the delineation of protonation and the complete description of the mechanism of acid catalyzed reactions.

Water molecule plays a crucial role in some chemical reactions.[1] In fact, adventitious water in reaction systems is essentially impossible to avoid, making the nature of mixed solvated proton ions [H(solvent)$_n$(H_2O)$_m$]$^+$ of particular interest. If the basicity of the solvents is lower than that of water molecule, the hydrated proton [H(H_2O)$_n$]$^+$ (*i. e.* solvated only by water) will be generated.[2] The structures of the hydrated protons are complex.[3] The clustering behavior of hydrated protons plays an important role in proton transfer reactions in chemical and biological systems[4] and in understanding charge transfer mechanisms and the properties of water.[5]

The stability of the solvated protons is highly related to the counterions. For example, the acid reagent [H(OEt_2)$_2$][B{$C_6H_3(CF_3)_2$}$_4$], a widely used acid in organotransition metal chemistry to produce active cations for catalysis, is barely stable thermally at room temperature.[6] In sharp contrast, the superacids [H(benzene)]-[1-H-$CB_{11}H_5X_6$] (X = halogen) are thermally stable to over 150 ℃ and have acidities which show many orders of magnitude higher than [H(OEt_2)$_2$]$^+$.[7] These results suggest that carborane anions are considerably more chemically inert and more thermally stable than other weakly coordinating anions.[2] Acids based on carborane anions should sustain much higher levels of acidity. We have recently developed a novel method of preparing highly halogenated carborane anions, 1-R-$CB_{11}Y_5X_6^-$ (X, Y = Cl, Br, I; R = H, Me) (**1**—**6** in Chart 1).[8,9] They are more chemically inert, more thermally stable and less coordi-

* E-mail: zxie@cuhk.edu.hk
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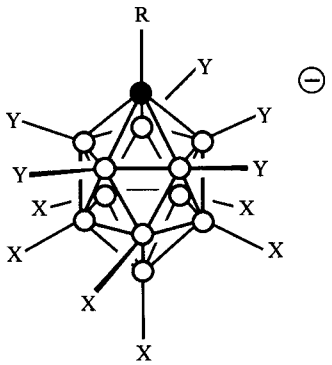
nating than the corresponding hexahalocarborane anions, 1-R-$CB_{11}Y_5X_6^-$. We report herein the syntheses and molecular structures of their solvated proton salts [H(solvent)$_n$][carborane] [carborane = 1-R-$CB_{11}Y_5X_6^-$ (X, Y = Cl, Br, I; R = H, Me), 1-H-$CB_9Br_9^-$] and protonation of alkene by the superacids H(1-R-$CB_{11}Y_5X_6$).

Chart 1 Carborane anions



1: 1-CH_3-$CB_{11}Br_{11}^-$ **4**: 1-H-$CB_9Br_9^-$
2: 1-H-$CB_{11}Br_{11}^-$ **5**: 1-H-$CB_{11}Cl_5Br_6^-$
3: 1-H-$CB_{11}Br_5Cl_6^-$ **6**: 1-H-$CB_{11}I_{11}^-$

Experimental

General procedures

Solvated protons are somewhat hydroscopic. Therefore, Schlenk and high-vacuum techniques were employed whenever necessary. Ag(1-R-$CB_{11}X_{11}$)[8] (R = Me, X = Br; R = H, X = Br, I), Ag(1-R-$CB_{11}Y_5X_6$) (R = H, Y = Br, Cl, X = Cl, Br),[9] and Ag(1-H-CB_9Br_9)[10] were prepared according to the reported methods. All other chemicals were purchased from Aldrich Chemical Co. and used as received unless otherwise noted. Infrared spectra were obtained from KBr pellets on a Nicolet Magna 550 Fourier transform spectrometer. Negative-ion matrix-assisted laser desorption/ionization (MALDI) MS spectra were recorded on a Bruker APEX FTMS spectrometer. Thermogravimetric analyses were performed on a TGA2950 thermogravimetric analyzer. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker 300 MHz DPX spectrometer at 300.13 and 75.47 MHz, respectively. ^{11}B NMR spectra were recorded on a Varian Inova 400 spectrometer at 128.32 MHz. All chemical shifts were reported in δ units with reference to the residual protons of deuterated solvent or external TMS for proton and carbon chemical shifts, and to external $BF_3 \cdot OEt_2$ for boron chemical shifts.

Preparation of [H_3O][1-CH_3-$CB_{11}Br_{11}$] ([H_3O][**1**])

To a dichloromethane solution (20 mL) of Ag[1-CH_3-$CB_{11}Br_{11}$] (0.15 g, 0.13 mmol) was slowly added 1 mol/L HCl aqueous solution until no more AgCl precipitate was formed (~0.15 mL of HCl was added) at room temperature. The resulting precipitate was filtered off and washed with dichloromethane (2 × 10 mL). The dichloromethane portions were combined and concentrated to give a pale yellow solid. Recrystallization from a 1,2-dichlorobenzene solution afforded [H_3O][**1**] as colorless crystals (0.11 g, 80%). ^{1}H NMR ($CDCl_3$) δ: 4.60 (br, 3H, H_3O), 1.80 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$) δ: 55.8 (cage C), 20.8 (CH_3); ^{11}B NMR ($CDCl_3$) δ: −4.97 (s, 1B), −11.37 (s, 5B), −12.63 (s, 5B); IR (KBr) ν: 3413 (br, m), 2956 (w), 2911 (w), 1639 (m), 1446 (m), 1087 (m), 988 (s) cm^{-1}; Negative-ion MALDI MS (isotopic abundance) calcd for 1-CH_3-$CB_{11}Br_{11}^-$: 1023 (90), 1024 (99), 1025 (100), 1026 (95), 1027 (82); found 1023 (92), 1024 (100), 1025 (95), 1026 (95), 1027 (80); TGA: 1.8% weight loss beginning at 239 ℃, calculated weight loss for one water molecule: 1.7%.

Preparation of [H_7O_3][1-H-$CB_{11}Br_{11}$] ([H_7O_3][**2**])

This compound was prepared as colorless crystals from Ag[1-H-$CB_{11}Br_{11}$] (0.20 g, 0.18 mmol) and 1 mol/L HCl in CH_2Cl_2 using procedures similar to those used in the synthesis of [H_3O][**1**]: yield 0.17 g (88%); ^{1}H NMR ($CDCl_3$) δ: 4.26 (br, 7H, H_7O_3), 2.88 (s, 1H, cage C-H); ^{13}C NMR ($CDCl_3$) δ: 57.3 (cage C); ^{11}B NMR ($CDCl_3$) δ: 1.42 (s, 1B), −5.32 (s, 5B), −9.16 (s, 5B); IR (KBr) ν: 3411 (br, m), 2959 (w), 2871 (w), 1703 (m), 1460 (m), 1088 (m), 988 (s) cm^{-1}; Negative-ion MALDI MS (isotopic abundance) calcd for 1-H-$CB_{11}Br_{11}^-$: 1009 (90), 1010 (99), 1011 (100), 1012 (94), 1013 (82), found 1009 (85), 1010 (100), 1011 (94), 1012 (92), 1013 (84); TGA: 1.9% weight loss beginning at

157 ℃, calculated weight loss for one water molecule: 1.7%.

Preparation of $[H_3O\cdot H_2O][1\text{-H-}CB_{11}Br_5Cl_6]$ ($[H_3O\cdot H_2O][\mathbf{3}]$)

This compound was prepared as colorless crystals from $Ag[1\text{-H-}CB_{11}Br_5Cl_6]$ (0.30 g, 0.35 mmol) and 1 mol/L HCl in CH_2Cl_2 using procedures similar to those used in the synthesis of $[H_3O][\mathbf{1}]$: yield 0.22 g (80%); ^{1}H NMR ($CDCl_3$) δ: 4.87 (br, 5H, H_3O + H_2O), 3.25 (s, 1H, cage C-H); ^{13}C NMR ($CDCl_3$) δ: 47.5 (cage C); ^{11}B NMR ($CDCl_3$) δ: 4.51 (s, 1B), −2.90 (s, 5B), −11.62 (s, 5B); IR (KBr) ν: 3540 (br, m), 3015 (w), 2918 (w), 1608 (m), 1106 (m), 1022 (s) cm^{-1}; Negative-ion MALDI MS (isotopic abundance) calcd for $1\text{-H-}CB_{11}Br_5Cl_6^-$: 741 (83), 742 (96), 743 (100), 744 (96), 745 (73); found 741 (77), 742 (91), 743 (100), 744 (98), 745 (82); TGA: 2.1% weight loss beginning at 83 ℃, calculated weight loss for one water molecule: 2.3%.

Preparation of $[H_9O_4][1\text{-H-}CB_9Br_9]$ ($[H_9O_4][\mathbf{4}]$)

This compound was prepared as colorless crystals from $Ag[1\text{-H-}CB_9Br_9]$ (0.20 g, 0.21 mmol) and 1 mol/L HCl in CH_2Cl_2 using procedures similar to those used in the synthesis of $[H_3O][\mathbf{1}]$: yield 0.16 g (89%); ^{1}H NMR ($CDCl_3$) δ: 5.53 (br, 9H, H_9O_4), 3.72 (s, 1H, cage C-H); ^{13}C NMR ($CDCl_3$) δ: 52.7 (cage C); ^{11}B NMR ($CDCl_3$) δ: 18.15 (s, 1B), −9.51 (s, 9B); IR (KBr) ν: 3439 (br, m), 3072 (w), 2907 (w), 1617 (m), 1529 (w), 1386 (w), 1087 (s), 988 (s), 829 (m), 538 (m) cm^{-1}; Negative-ion MALDI MS (isotopic abundance) calcd for $1\text{-H-}CB_9Br_9^-$: 827 (75), 828 (97), 829 (100), 830 (90), 831 (70); found 827 (82), 828 (95), 829 (100), 830 (97), 831 (85); TGA: 9.2% weight loss beginning at 79 ℃, calculated weight loss for four water molecules: 10.1%.

Preparation of $[H\{(CH_3)_2NCHO\}(H_2O)][1\text{-H-}CB_{11}Cl_5Br_6]$ ($[H(DMF)(H_2O)][\mathbf{5}]$)

To a dichloromethane solution (15 mL) of $Ag[1\text{-H-}CB_{11}Cl_5Br_6]$ (0.30 g, 0.33 mmol) was slowly added 1 mmol/L HCl aqueous solution until no more AgCl precipitate was formed (~0.4 mL of HCl was added) at room temperature. The resulting precipitate was filtered off and washed with dichloromethane (2 × 10 mL). The dichloromethane portions were combined and concentrated to give a pale yellow solid. Recrystallization from a *N*,*N*-dimethylformamide solution to afford $[H(DMF)\cdot(H_2O)][\mathbf{5}]$ as colorless crystals (0.26 g, 89%). ^{1}H NMR ($CDCl_3$) δ: 8.00 [s, 1H, $(CH_3)_2NC\mathbf{H}O$], 3.95 (s, 2H, H_2O), 2.95 [s, 3H, $(C\mathbf{H}_3)_2NCHO$], 2.75 [s, 3H, $(C\mathbf{H}_3)_2NCHO$]; ^{13}C NMR ($CDCl_3$) δ: 161.46 [$(CH_3)_2N\mathbf{C}HO$], 55.18 (cage C), 36.41, 31.85 [$(\mathbf{C}H_3)_2NCHO$]; ^{11}B NMR ($CDCl_3$) δ: −6.26 (s, 1B), −11.12 (s, 5B), −13.22 (s, 5B); IR (KBr) ν: 3350 (w), 3040 (m), 2957 (w), 2912 (w), 1615 (m), 1119 (s), 1062 (m), 980 (s) cm^{-1}; Negative-ion MALDI MS (isotopic abundance) calcd for $1\text{-H-}CB_{11}Cl_5Br_6^-$: 786 (81), 787 (89), 788 (100), 789 (96), 790 (88); found 786 (84), 787 (96), 788 (100), 789 (96), 790 (86); TGA: 2.5% weight loss beginning at 105 ℃, calculated weight loss for one water molecule: 2.1%.

Preparation of $[H\{(CH_3CH_2)_2O\}(H_2O)][1\text{-H-}CB_{11}I_{11}]\cdot H_2O$ ($[H(OEt_2)(H_2O)][\mathbf{6}]\cdot H_2O$)

This compound was prepared as colorless crystals from $Ag[1\text{-H-}CB_{11}I_{11}]$ (0.30 g, 0.18 mmol) and 1 mol/L HCl in CH_2Cl_2 using procedures similar to those used in the synthesis of $[H(DMF)(H_2O)][\mathbf{5}]$ except recrystallization from a ether solution: yield 0.27 g (89%); ^{1}H NMR ($CDCl_3$) δ: 4.62 (s, 5H, H_2O), 3.66 [q, J = 6.0 Hz, 4H, $(CH_3C\mathbf{H}_2)_2O$], 1.17 [t, J = 6.0 Hz, 6H, $(C\mathbf{H}_3CH_2)_2O$]; ^{13}C NMR ($CDCl_3$) δ: 66.48 [$(CH_3\mathbf{C}H_2)_2O$], 62.9 (cage C), 18.55 [$(\mathbf{C}H_3CH_2)_2O$]; ^{11}B NMR ($CDCl_3$) δ: −9.01 (s, 1B), −13.6 (s, 5B), −20.3 (s, 5B); IR (KBr) ν: 3365 (w), 3040 (br), 2999 (m), 2955 (m), 2913 (m), 1606 (m), 1381 (s), 1093 (s), 915 (s) cm^{-1}; Negative-ion MALDI MS (isotopic abundance) calcd for $1\text{-H-}CB_{11}I_{11}^-$: 1527 (37), 1528 (75), 1529 (100), 1530 (81), 1531 (30); found 1527 (35), 1528 (75), 1529 (100), 1530 (83), 1531 (33); TGA: 5.0% weight loss beginning at 122 ℃, calculated weight loss for one water molecule and one diethyl ether molecules: 5.7%.

Reaction of H(1-H-$CB_{11}Br_5Cl_6$) *with cyclohexene*

[$H_3O \cdot H_2O$][**3**] (0.20 g, 0.26 mmol) was heated at 200 ℃ under high vacuum (1 Pa) for 4 h affording presumably H(1-H-$CB_{11}Br_5Cl_6$) as a white solid. Dry cyclohexene (0.50 g, 6.10 mmol) was transferred into this reaction vessel and the mixture was stirred at room temperature overnight, then quenched with water and extracted with Et_2O. The organic layer was analyzed by GC/MS. Cyclohexanol was detected and the conversion yield was 45% based on [$H_3O \cdot H_2O$][**3**].

X-Ray structure determination

All single crystals were immersed in Paraton-N oil and then sealed in thin-walled glass capillaries. Data were collected at 293 K either on a MSC/Rigaku RAXIS-IIC imaging plate or on a Rigaku AFC7R diffractometer using Mo Kα radiation (0.071073 nm) from a Rigaku rotating-anode X-ray generator operating at 50 kV and 90 mA. An absorption correction was applied by correlation of symmetry-equivalent reflections using the ABSCOR program[11] or by using an empirical Ψ-scan method. All structures were solved by direct methods and subsequent Fourier difference techniques and refined anisotropically for all non-hydrogen atoms by full-matrix least-squares calculations on F^2 using SHELXTL V 5.03 program package (PC version).[12] The hydrogen atoms were geometrically fixed using the riding model. Most of water hydrogen atoms could not be located. In the solid-state structure of [H_3O][**1**], the exohedral Me group is completely mixed with the 11 Br atoms of the cage anion. Each of the six independent Br atoms is assigned an SOF of 0.931, which is calculated from the equation $(6 + 11 \times 35)/(12 \times 35)$. In the solid-state structure of [$H_3O \cdot H_2O$][**3**], the cage C and B atoms are indistinguishable, and the exohedral H atom is completely scrambled with the 5 Br and 6 Cl atoms. Each of the two independent Br atoms is assigned an SOF of 0.662, which is calculated from the equation $(1 + 6 \times 17 + 5 \times 35)/(12 \times 35)$. Crystal data and details of data collection and structure refinement were given in Tables 1 and 2, respectively.

Table 1 Crystal data and summary of data collection and refinement for [H_3O][**1**], [H_7O_3][**2**] and [$H_3O \cdot H_2O$][**3**]

	[H_3O][**1**]	[H_7O_3][**2**]	[$H_3O \cdot H_2O$][**3**]
Formula	$C_2H_6B_{11}Br_{11}O$	$CH_8B_{11}B_{11}O_3$	$CH_6B_{11}Br_5Cl_6O_2$
Crystal size (mm)	0.23 × 0.18 × 0.07	0.26 × 0.18 × 0.16	0.20 × 0.20 × 0.20
F. W.	1043.99	1065.99	781.22
Crystal system	triclinic	monoclinic	trigonal
Space group	$P(-1)$	$P2_1/n$	$R(-3)$
a (nm)	0.9210(6)	1.0794(8)	0.9510(1)
b (nm)	0.9224(5)	1.8735(11)	0.9510(1)
c (nm)	0.9224(4)	1.3049(7)	2.1573(4)
α (°)	63.39(2)	90	90
β (°)	63.22(3)	99.96(6)	90
γ (°)	63.06(4)	90	120
V (nm^3)	0.5936(6)	2.599(3)	1.6896(5)
Z	1	4	3
D_{calcd} (Mg/m^3)	2.920	2.724	2.303
2θ range (°)	5.2 to 50.0	3.8 to 50.0	5.3 to 50.0
μ (mm^{-1})	18.533	16.958	9.627
F(000)	466	1912	1080
No. of obsd reflns	1682	2581	501
No. of params refnd	119	245	41
Goodness of fit	1.088	1.078	1.133
R_1	0.088	0.068	0.079
wR_2	0.227	0.171	0.192

Table 2 Crystal data and summary of data collection and refinement for $[H_9O_4][4]$, $[H(DMF)(H_2O)][5]$ and $[H(OEt_2)(H_2O)][6]\cdot H_2O$

	$[H_9O_4][4]$	$[H(DMF)(H_2O)][5]$	$[H(OEt_2)(H_2O)][6]\cdot H_2O$
Formula	$CH_{10}B_9Br_9O_4$	$C_4H_{11}B_{11}Br_6Cl_5NO_2$	$C_5H_{16}B_{11}I_{11}O_3$
Crystal size (mm)	0.20×0.18×0.10	0.20×0.20×0.10	0.50×0.20×0.15
F. W.	902.57	880.76	1638.99
Crystal system	monoclinic	triclinic	monoclinic
Space group	$P2_1/c$	$P(-1)$	Cc
a (nm)	1.3246(7)	1.0326(2)	1.0050(2)
b (nm)	1.0501(3)	1.3687(3)	1.7862(4)
c (nm)	1.7595(6)	2.7362(6)	1.7118(3)
α (°)	90	87.85(3)	90
β (°)	109.22(5)	89.08(3)	92.85(3)
γ (°)	90	81.64(3)	90
V (nm^3)	2.311(1)	3.8232(1)	3.0691(11)
Z	4	6	4
D_{calcd} (Mg/m^3)	2.594	2.295	3.547
2θ range (°)	3.2 to 52.0	3.4 to 50.0	4.6 to 50.0
μ (mm^{-1})	15.612	9.981	11.113
$F(000)$	1632	2448	2832
No. of obsd reflns	4525	4970	2902
No. of params refnd	258	793	272
Goodness of fit	0.832	1.114	1.071
R_1	0.040	0.109	0.079
wR_2	0.093	0.291	0.194

Results and discussion

Synthesis and characterization

Silver(I) salts of carborane anions are very useful reagents for the production of various cations.[2,13] Treatment of Ag(carborane) with slightly excess hydrochloric acid in CH_2Cl_2 at room temperature gives, after removal of AgCl precipitate and CH_2Cl_2, a pale yellow solid. Recrystallization from a 1,2-dichlorobenzene solution affords the hydrated proton salts of carborane anions $[H(H_2O)_n][carborane]$ as colorless crystals in 79%—89% yields. Recrystallization from a diethyl ether (Et_2O) or *N*,*N*-dimethylformamide (DMF) solution produces the mixed solvated proton salts $[H(solvent)(H_2O)][carborane]$. These results are summarized in Table 3.

These solvated proton salts are somewhat hydroscopic. The transparent crystals will become non-transparent ones after exposure to air for a few minutes. They are very soluble in polar organic solvents such as THF, acetone, Et_2O, DMF and acetic acid, soluble in water, sparely soluble in toluene and insoluble in *n*-hexane. They were characterized by ^1H, ^{13}C and ^{11}B NMR, IR, negative-ion MS spectroscopy and thermogravimetric analyses (TGA). Their molecular structures were confirmed by single-crystal X-ray analyses. It is noted that elemental analyses are not accurate due to the incomplete combustion of highly halogenated carborane anions.[8-10]

The ^{11}B NMR spectra of the solvated proton salts are identical to those of silver(I) salts Ag(carborane), indicating that the carborane anions remain intact during the reactions. This result was confirmed by the negative-ion MALDI MS spectroscopic data. The proton chemical shifts of $[H(H_2O)_n]^+$ are assigned via H/D exchange experiments with D_2O.

The thermal stability of these solvated proton salts is examined by TGA technique. The results show that they are stable at > 80 ℃ and also offer useful information on water contents of the salts.

Table 3 Synthesis of solvated protons incorporating weakly coordinating anions

$$Ag(carborane) \xrightarrow[-AgCl]{HCl/solvent} [H(solvent)_n][carborane]$$

Cation	Anion	Salt
H_3O^+	1-CH_3-$CB_{11}Br_{11}^-$ (**1**)	$[H_3O][\mathbf{1}]$
$H_7O_3^+$	1-H-$CB_{11}Br_{11}^-$ (**2**)	$[H_7O_3][\mathbf{2}]$
$[H_3O\cdot H_2O]^+$	1-H-$CB_{11}Br_5Cl_6^-$ (**3**)	$[H_3O\cdot H_2O][\mathbf{3}]$
$H_9O_4^+$	1-H-$CB_9Br_9^-$ (**4**)	$[H_9O_4][\mathbf{4}]$
$[H(DMF)(H_2O)]^+$	1-H-$CB_{11}Cl_5Br_6^-$ (**5**)	$[H(DMF)(H_2O)][\mathbf{5}]$
$[H(Et_2O)(H_2O)]^+$	1-H-$CB_{11}I_{11}^-$ (**6**)	$[H(Et_2O)(H_2O)][\mathbf{6}]$

Reactivity

The acidity of Brønsted acid HY is dependent upon the coordinating ability of the counterion Y^-. The less coordinating the anion Y^- is, the stronger HY is.[2] It is reasonable to suggest that H(carborane) is a superacid since carborane anions are the least coordinating anions presently known.[2] TGA results show that the solvated organic molecules or water in the cation $[H(solvent)_n]^+$ can be removed under high vacuum and high temperature conditions to give a white solid with very strong acidity presumably forming H(carborane).[14] This material can protonate cyclohexene to give, after hydrolysis, cyclohexanol.

Solid-state structure

The molecular structure of $[H_3O][\mathbf{1}]$ derived from single-crystal X-ray analyses is shown in Fig. 1. The C—Me and B—Br vertexes in 1-CH_3-$CB_{11}Br_{11}^-$ (**1**) are indistinguishable due to the crystallographically imposed *i* symmetry, and they are represented by six independent B—Br vertexes. The average B—Br distance of 0.1966(9) nm falls in a range of 0.192—0.200 nm normally observed in polybromocarborane anions.[8-10] The closest cation/anion O···Br distance is 0.3535 nm, indicative of very weak, if rather directionless, H-bonding between cations and anions.[15] The cations and anions are discrete in this structure. This can be compared to the structure of $[H_3O][AsF_6]$ where strong H-bonding to fluorine is observed and believed to stabilize the pyramidal H_3O^+ ion.[16]

Fig. 2 shows the crystal structure of $[H_7O_3][\mathbf{2}]$ consisting the discrete cations $H_7O_3^+$ and anions 1-H-$CB_{11}Br_{11}^-$ (**2**) with the closest O···Br contact of 0.3472 nm. The central H_3O^+ ion is surrounded by two water molecules with the O(3)-O(2)-O(1) angle of 111.1(5)°.

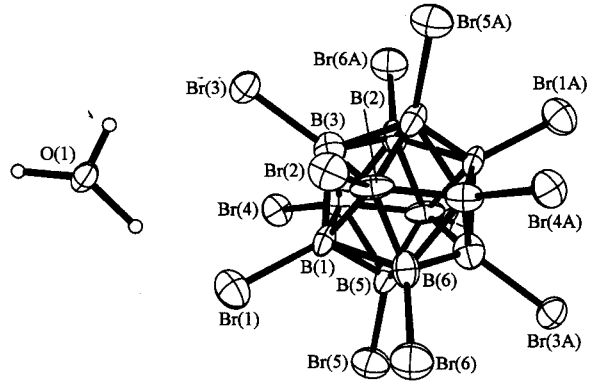


Fig. 1 Molecular structure of $[H_3O][\mathbf{1}]$. Note that the exohedral Me group is completely mixed with the 11 Br atoms of the cage anion.

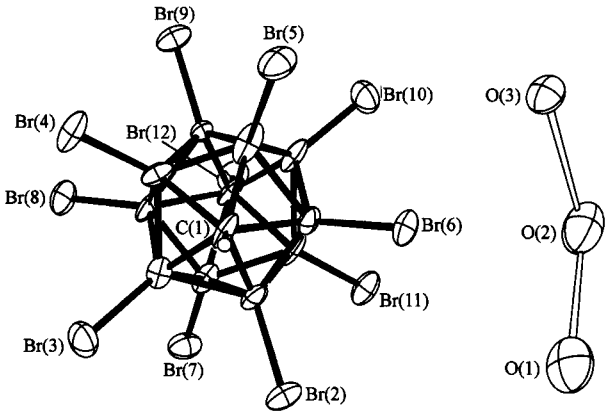


Fig. 2 Molecular structure of $[H_7O_3][\mathbf{2}]$. Selected bond distances (nm) and angles (°): O(1)—O(2) 0.2547(9), O(2)—O(3) 0.2600(9), O(1)-O(2)-O(3) 111.1(5).

The O···O distances of 0.2547(9) and 0.2600(9) nm fall in the range of 0.245—0.260 nm observed for hydrated proton ions.[3] This structure can be compared to the non-discrete molecules $HY(H_2O)_3$(Y = Br^-, ClO_4^- and NO_3^-) where $H_7O_3^+$ ions are discernible entities within the H-bonded arrays.[3]

The molecular structure of $[H_3O\cdot H_2O][\mathbf{3}]$ is shown in Fig. 3. The O(1)···O(1A) distance of 0.2704(3) nm is too long for H-bonding.[3] Therefore, this cation is better described as $[H_3O\cdot H_2O]^+$ rather than $[H_5O_2]^+$. The closest O···Br contact of 0.3541 nm suggests that the cation and anion are discrete in the structure. The anion has crystallographically imposed C_3 symmetry, which prohibits differentiation of the carbon atom from the boron atoms within the cage. The cage H atom is thus completely scrambled with the five Br and six Cl atoms, the cage is represented by only two independent B—Br vertexes.

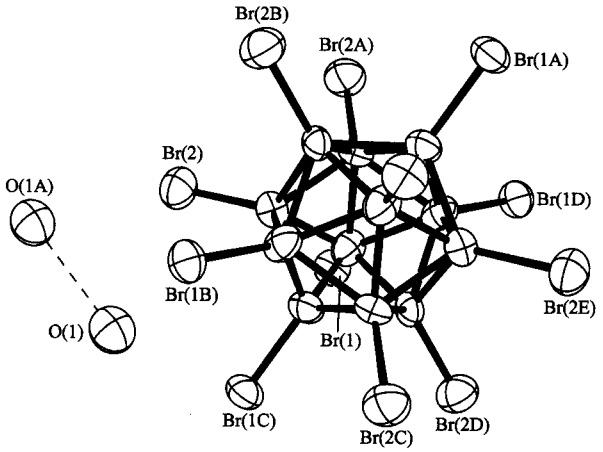


Fig. 3 Molecular structure of $[H_3O\cdot H_2O][\mathbf{3}]$. Note that the cage H atom is completely scrambled with the five Br and six Cl atoms.

Fig. 4 shows the solid-state structure of $[H_9O_4][\mathbf{4}]$ consisting of discrete cations $H_9O_4^+$ and anions 1-H-$CB_9Br_9^-$ (**4**) with the closest O···Br contact of 0.3498 nm.

The geometry of **4** is the same as that observed in $(\eta^2\text{-}C_6H_6)Ag(1\text{-}H\text{-}CB_9Br_9)$.[10] The O···O distances range from 0.2465(3) nm to 0.2532(3) nm and the O···O···O angles are within the range of 110.9(1)°—113.9(1)°. The central H_3O^+ ion is hydrated by three water molecules with O—H···O hydrogen bonding in a pyramidal arrangement, which is very similar to that found in $[H_9O_4][1\text{-}H\text{-}CB_{11}H_5Br_6]$.[15]

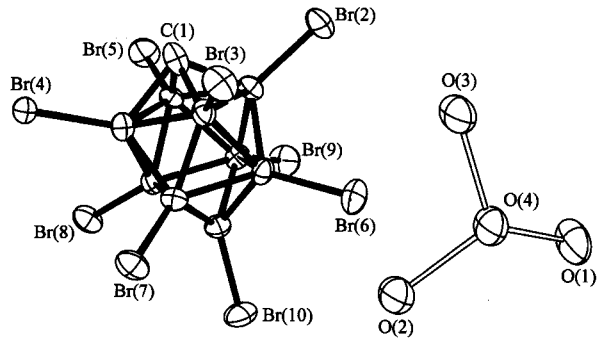


Fig. 4 Molecular structure of $[H_9O_4][\mathbf{4}]$. Selected bond distances (nm) and angles (°): O(4)—O(1) 0.2500 (3), O(4)—O(2) 0.2532(3), O(4)—O(3) 0.2465(3), O(1)-O(4)-O(3) 113.9(1), O(1)-O(4)-O(2) 110.9(1), O(2)-O(4)-O(3) 111.6(1).

Replacement of one water molecule in $H_5O_2^+$ generates the mixed solvated proton ion [H(H_2O)(solvent)]$^+$. Fig. 5 illustrates the molecular structure of [H-(DMF)(H_2O)][**5**], one of three crystallographically independent molecules in the unit cell. The O···O distances are 0.243(2), 0.245(2) and 0.250(2) nm, suggestive of a strong O···H···O bonding. The C = O bond distances in the cation are 0.131(2), 0.131(1) and 0.126(2) nm, which are significantly longer than the value of 0.1230(1) nm found in free DMF,[17] indicative of a substantial degree of protonation. The geometry of 1-H-$CB_{11}C_{l5}Br_6^-$ (**5**) is the same as that in (η^1-mesitylene)-Ag(1-H-$CB_{11}C_{l5}Br_6$).[9]

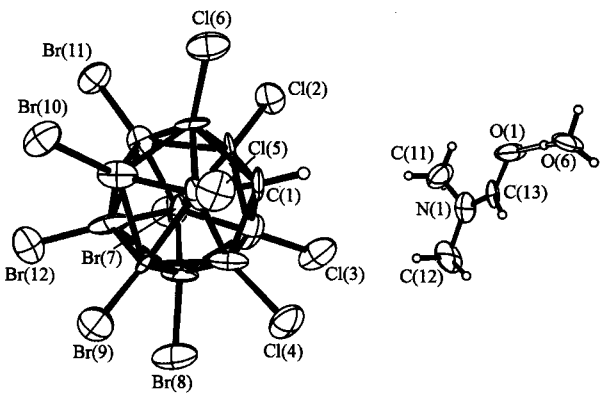


Fig. 5 Molecular structure of [H(DMF)(H_2O)][**5**], showing one of three crystallographically independent molecules in the unit cell. Selected bond distances (nm): O(6)—O(1) 0.243(2) [0.245(2), 0.250(2)], O(1)—C(13) 0.131(2) [0.131(1), 0.126(2)]. Distances in brackets are those of the other two molecules.

Fig. 6 shows the solid-state structure of another mixed solvated ion salt $[H(Et_2O)(H_2O)][\mathbf{6}]$. There is one water molecule in the crystal lattice showing no interactions with the cations and the anions. The O(1)···O(3) separation of 0.242(3) nm suggests a strong O(1)···H···O(3) bonding

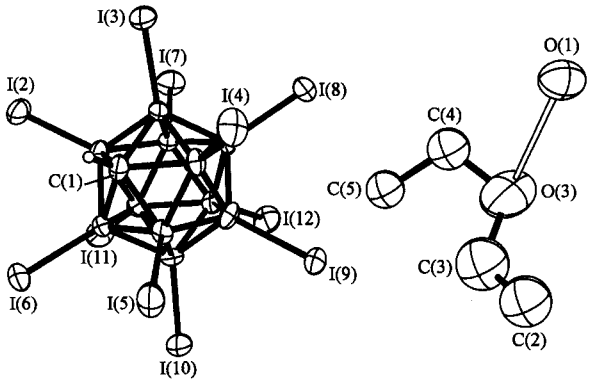


Fig. 6 Molecular structure of $[H(OEt_2)(H_2O)][\mathbf{6}]$ (the water molecule in the crystal lattice is not shown).

Conclusion

Six new solvated proton salts of highly halogenated carborane anions were prepared from the salt metathesis reaction of Ag(carborane) and HCl in high yields. Single-crystal X-ray analyses show that they are all discrete molecules, which is unique to carborane anion chemistry. The number of the solvated water molecules surrounding H_3O^+ ion can not be determined with the knowledge of the size and substituents of the carborane anions.

The prepared $[H(solvent)_n][carborane]$ salts provide convenient weighable sources of Brønsted acid reagents having a wide range of acidities and good thermal stabilities. TGA results indicate that the solvated solvents (water or organic molecules) in the cations $[H(solvent)_n]^+$ can be removed under thermal and high vacuum conditions to give superacidic materials H(carborane) which can protonate olefin.

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