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Structural chemistry of halogenated monocarbaboranes: the extended structures of Cs[1-$HCB_9H_4Br_5$], Cs[1-$HCB_{11}H_5Cl_6$] and Cs[1-$HCB_{11}H_5Br_6$]

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The crystal structures of the Cs^+ salts of the halogenated monocarbaborane anions [*closo*-1-$HCB_9H_4Br_5$]$^-$, [*closo*-1-$HCB_{11}H_5Cl_6$]$^-$ and [*closo*-1-$HCB_{11}H_5Br_6$]$^-$ have been determined. The structures show two-dimensional extended-sheet or three-dimensional lattice structures and feature unusual distorted cuboctahedral and tetrakis hexahedral coordination geometries about Cs^+. Incidental to the structural work, new convenient preparations of the precursive non-halogenated monocarbaborane anions [*closo*-1-HCB_9H_9]$^-$ and [*closo*-1-$HCB_{11}H_{11}$]$^-$ are presented.

Introduction

Monocarbaborane cluster chemistry is sparsely investigated compared to its flanking fields of binary boron hydride cluster chemistry on one hand, and dicarbaborane cluster chemistry on the other.[1,2] Reasons for this include that entry into dicarbaborane chemistry *via* the addition of alkynes to *nido*-decaborane, $B_{10}H_{14}$, is relatively easy. By contrast, entries into monocarbaborane chemistry have been more difficult, relying principally on one-carbon dismantling reactions from dicarbaboranes,[3] or on cyanide or organyl cyanide addition to borane residues to give C-aminated monocarbaboranes[4] which then generally must involve subsequent complex C-deamination protocols for further monocarbaborane chemistry.[2]

However, new synthetic breakthroughs to the monocarbaboranes *via* the Brellochs reaction of aldehydes with *nido*-$B_{10}H_{14}$ now presage an accelerating expansion of the area.[5] This is timely, as there is now considerable contemporary interest in monocarbaborane chemistry, from the points of view of (a) its general development,[5] (b) the development of metallamonocarbaborane chemistry,[2,6] (c) the preparation of ionic liquids,[7] (d) aspects of liquid-crystal chemistry and other rheological applications,[8] (e) potential for rigid zwitterions of high dipolarities and hyperpolarisabilities,[9] (f) building blocks for 'molecular meccano' or 'molecular tinkertoy' nano-architectural chemistries,[10] and (g) the tailoring of compounds for host–guest 'molecular recognition' and supramolecular assembly.[11] Of particular contemporary interest are the *closo* ten-vertex [1-HCB_9H_9]$^-$ and *closo* twelve-vertex [$HCB_{11}H_{11}$]$^-$ anions and their alkylated or halogenated derivatives.[12–14] These anions possess chemical, electrochemical and thermal stability, and the anionic charge is highly delocalised, so that they have use in 'least-coordinating-anion' chemistry for the study of systems of high Lewis acidity,[2,12] for example in applications in cationic metallocene catalysis,[15] and in the stabilisation of both coordinatively unsaturated cations[16] and of strong Brønsted acids.[17]

The halogenated monocarbaborane anions have attracted particular interest in this last context. However, while regarded as weakly coordinating, they are nevertheless known to exhibit coordinate interactions with transition-element centres in the solid state, and in some instances these interactions may persist into the solution state.[18–22] The few known examples include B–Br···Ag,[18,19] B–Cl···Ag,[18] B–Br···Fe(II),[20] and B–Br···Mo interactions,[21] as well as agostic B–H···Ag interactions.[19,22] Complementary to these transition-element examples, it is of interest to examine for any coordinating ability of the halogenated monocarbaborane anions towards non-transition-element centres with minimal back-bonding tendencies. For example, any interaction with the Cs^+ cation is of particular significance here because borane-cluster anions have use as radiocaesium precipitation agents in nuclear-waste processing.[23] The structures of the Cs^+ salts of the polyhalogenated monocarbaborane anions [1-HCB_9Br_9]$^-$,[24] [$HCB_{11}Br_5I_6$]$^-$,[18] [$HCB_{11}Br_{11}$]$^-$,[14] and [$HCB_{11}H_{10}Br$]$^-$ [25] have been previously reported. In all cases, closest-contact B–Br···Cs^+ and B–H···Cs^+ interactions occur, but the 'long' B–Br···Cs^+ and B–H···Cs^+ distances observed indicate that the compounds can principally be regarded in terms of ionic salts. The interionic assembly patterns observed range from quasi-one-dimensional (1D) chain structures[24] to three-dimensional (3D) lattices,[18,25] and the Cs^+ cations are observed to exhibit coordination numbers as high as twelve, though often there is little relationship to conventional regular coordination geometries. Interest in the structural behaviour of these halogenated monocarbaborane anions towards centres such as Cs^+ has recently been given further impetus by their incorporation into crystalline supramolecular materials in which they exhibit coordinative interactions with Group 1 metal cations.[26] Thus, for example, coordinate interactions between monocarbaborane B–X

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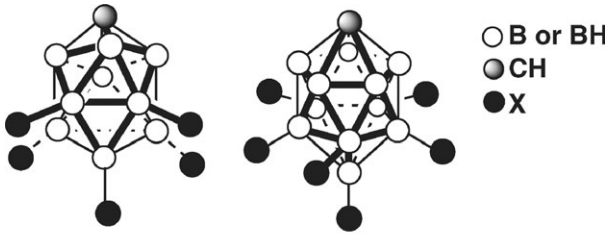
groups and the Na^+, K^+, Rb^+ and Cs^+ cations have recently been documented for crystalline arrays involving the host-molecule cyclotriveratrylene.[26] It is of additional interest, therefore, to examine the fundamental basic coordination modes between these types of anions and the Cs^+ cation in the absence of the supramolecular assembly components that engender the more complex supramolecular aggregations.



$[CB_9H_5Br_5]^-$ **1** $[CB_{11}H_6X_6]^-$ X = Cl **2**; Br **3**

In order to contribute to knowledge germane to these various areas, we report herein the crystal structures of the Cs^+ salts **1a**, **2a** and **3a** of the [*closo*-1-$HCB_9H_4Br_5$]$^-$ anion **1**, the [*closo*-1-$HCB_{11}H_5Cl_6$]$^-$ anion **2** and the [*closo*-1-$HCB_{11}H_5Br_6$]$^-$ anion **3**, as determined by single-crystal X-ray diffraction analyses. As part of this report we also take the opportunity to communicate convenient new, refined, syntheses of the precursive non-halogenated *closo* monocarbaborane anions [*closo*-1-HCB_9H_9]$^-$ and [*closo*-$HCB_{11}H_{11}$]$^-$, both prepared *via* the [*arachno*-6-$H_2CB_9H_{12}$]$^-$ anion, in turn prepared by the Brellochs procedure[5] from *nido*-$B_{10}H_{14}$ and formaldehyde, HCHO.

Experimental

Synthesis

The starting unsubstituted anions [*closo*-1-HCB_9H_9]$^-$ and [*closo*-$HCB_{11}H_{11}$]$^-$ were prepared *via* the [*arachno*-6-$H_2CB_9H_{12}$]$^-$ anion obtained from *nido*-$B_{10}H_{14}$ and HCHO by the Brellochs reaction,[5] according to the following previously unpublished procedures; *nido*-$B_{10}H_{14}$ and other reagents were obtained commercially. NMR spectroscopy was performed at 294–299 K and at *ca.* 5.9 T and 11.75 T (fields corresponding to 250 and 500 MHz ^{1}H frequencies respectively) using commercially available instrumentation and using techniques and procedures adequately described and enunciated elsewhere.[27–29] Chemical shifts, δ, are given in ppm relative to Ξ = 100 MHz for $\delta(^1H)$ (±0.05 ppm) (nominally TMS), Ξ = 32.083 972 MHz for $\delta(^{11}B)$ (±0.5 ppm) (nominally [$BF_3(OEt_2)$] in $CDCl_3$)[28] and Ξ = 25.145 004 MHz for $\delta(^{13}C)$ (±0.5 ppm) (nominally TMS). Ξ is as defined by McFarlane and is the resonance frequency of a nucleus in the polarising field B_0 in which the protons of TMS resonate at exactly 100 MHz.[29]

Preparation of [NEt_4][*arachno*-6-$H_2CB_9H_{12}$] from $B_{10}H_{14}$ and HCHO in alkaline solution. A solution of KOH (10 g, 0.18 mol) in H_2O (150 ml) was added to $B_{10}H_{14}$ (6.0 g, 49.1 mmol) at 0 °C. Then, over a period of 6 h, HCHO (37% solution in water, stabilized with 10% MeOH; 40 ml, corresponding to 510 mmol HCHO) was added in five portions at approximately equal intervals. The reaction mixture was then stirred overnight, the MeOH was removed under reduced pressure and additional H_2O (100 ml) was added. The alkaline solution was extracted three times with Et_2O (3 × 100 ml), and H_2O (300 ml) was added to the combined ether extracts. The Et_2O was removed under reduced pressure and [NEt_4]Cl (10 g, 60 mmol) was added to the resulting aqueous solution. A colourless precipitate was formed, which was filtered off, washed with water (3 × 50 ml) and dried *in vacuo* to yield [NEt_4][*arachno*-6-$H_2CB_9H_{12}$] as a white crystalline solid (9.2 g, 36.3 mmol, 74%). NMR, $(CD_3)_2CO$ at 294–299 K, ordered as assignment $\delta(^{11}B)$ (ppm) [$\delta(^1H)$ (ppm) in square brackets]: BH(9) −1.3 [+2.32], BH(8) −10.3 [+2.02], BH(5,7,10) −12.8 [+2.17], BH(2) −22.6 [+0.95], BH(1,3) −28.5 [+0.79] and BH(4) −39.6 [+0.34] with $\delta(^1H)$ for μ-H(7,8) and μ-H(5,10) at −3.94 and μ-H(9) at −1.99 and μ-H(10) at −0.21 ppm; additionally $\delta(^1H)$(Et) at +3.49 (8H, quartet), +1.41 (12H, triplet) ppm, with $\delta(^{13}C)$(cluster) −4.5, and $\delta(^{13}C)$(Et) +7.9 and +47.6 ppm.

Preparation of [NEt_4] [*closo*-2-HCB_9H_9] from the reaction of the [*arachno*-6-$H_2CB_9H_{12}$]$^-$ anion with I_2 in alkaline solution. A solution of [NEt_4][*arachno*-6-$H_2CB_9H_{12}$] (3.04 g, 12.0 mmol) in aqueous HCl (5%, 160 ml) was extracted with Et_2O (3 × 80 ml). The separated organic layers were then shaken with aqueous KOH (1.0 M; 400 ml), and the Et_2O evaporated under reduced pressure. Elemental I_2 (4.0 g, 15.8 mmol) was added to the resulting alkaline aqueous solution, which was then stirred for 2 h at ambient temperature. [NEt_4]Cl (3.32 g, 20 mmol) was added, and, after brief stirring, the colourless precipitate was filtered off, washed with H_2O (3 × 50 ml) and dried *in vacuo*, to yield [NEt_4][*closo*-2-HCB_9H_9] as a white microcrystalline solid (2.76 g, 11.0 mmol, 92%). NMR, $(CD_3)_2CO$ at 299 K, ordered as assignment $\delta(^{11}B)$ (ppm) [$\delta(^1H)$ (ppm)]: BH(10) −0.0 [+3.74], BH(1) −7.4 [+3.53], BH(4) −23.0 [+1.08], BH(6,9) −30.2 [+0.61], BH(3,5) −32.2 [+1.05] and BH(7,8) −32.2 [+0.32]; additionally $\delta(^1H)$(Et) at +3.48 (8H, quartet), +1.39 (12H, triplet) and $\delta(^1H)$(cluster) +2.05 ppm, with $\delta(^{13}C)$(cluster) +26.6, and $\delta(^{13}C)$(Et) +7.8 and +47.6 ppm.

Preparation of the $[NEt_4]^+$ and Cs^+ salts of the [*closo*-1-HCB_9H_9]$^-$ anion *via* the thermal isomerisation of [NEt_4] [*closo*-2-HCB_9H_9]. [NEt_4][*closo*-2-HCB_9H_9] (2.0 g, 8.0 mmol) in dimethoxyethane (DME) (30 ml) was heated for 24 h under reflux. The solution was allowed to cool to room temperature and the DME was removed under reduced pressure. After adding H_2O (50 ml) and aqueous HCl (10%, 150 ml) the mixture was extracted with Et_2O (3 × 80 ml). H_2O (100 ml) was added to the combined Et_2O extracts, and the Et_2O was removed under reduced pressure. The aqueous solution was filtered, and [NEt_4]Cl (2.0 g, 12 mmol) was added to the filtrate. The resulting white precipitate was filtered off, and dried *in vacuo* to yield [NEt_4][*closo*-1-HCB_9H_9] (1.9 g, 7.6 mmol, 94%). Cs[*closo*-1-HCB_9H_9] was obtained in similar yield by use of excess CsCl, rather than excess [NEt_4]Cl, as the precipitating agent. NMR of [NEt_4][*closo*-1-HCB_9H_9], $(CD_3)_2CO$ at 299 K, ordered as assignment $\delta(^{11}B)$ (ppm) [$\delta(^1H)$ (ppm)]: BH(10) +29.9 [+5.87], BH(2,3,4,5) −19.5 [+1.73] and BH(6,7,8,9) −25.0 [+0.90]; additionally $\delta(^1H)$(Et) at +3.50 (8H, quartet), +1.41 (12H, triplet) and $\delta(^1H)$(cluster) +4.63 ppm, with $\delta(^{13}C)$(cluster) +52.8, and $\delta(^{13}C)$(Et) +52.5 and +7.1 ppm.

Preparation of $[NEt_4]^+$ and Cs^+ salts of the [*closo*-1-$HCB_{11}H_{12}$]$^-$ anion from the reaction of the [*arachno*-6-$H_2CB_9H_{14}$]$^-$ anion with [$BH_3(SMe_2)$]. [NEt_4][*arachno*-6-$H_2CB_9H_{12}$] (4.6 g, 18.2 mmol) was dissolved in 1,2-$Cl_2C_2H_4$ (50 ml). [$BH_3(SMe_2)$] (40 ml, 430 mmol) was added and the mixture was heated under reflux for 4 d. After cooling to 0 °C, H_2O (50 ml) was added slowly, and then aqueous HCl (10%, 150 ml). Following removal of the 1,2-$Cl_2C_2H_4$ under reduced pressure, the remaining precipitate was filtered off and dried *in vacuo*. Aqueous HCl (10%, 500 ml) was added to the colourless solid, and the mixture was extracted with Et_2O (3 × 150 ml). H_2O (400 ml) was added to the combined ethereal extracts, and the Et_2O was then evaporated under reduced pressure. The remaining aqueous solution was filtered, and [NEt_4]Cl (4.14 g, 25 mmol) was added to the filtrate. The colourless precipitate was filtered off, and dried *in vacuo*. To remove traces of SMe_2-containing by-products (evident from mass spectrometry), the crude

product was dissolved in the minimum volume of hot ethanol; on cooling, a white precipitate resulted, which was filtered off, and dried *in vacuo*, to yield [NEt_4][*closo*-$HCB_{11}H_{11}$] as a white crystalline solid (4.41 g, 16.2 mmol, 89%). Cs[*closo*-$HCB_{11}H_{11}$] was obtained in similar yield by use of excess CsCl, rather than excess [NEt_4]Cl, as the precipitating agent. NMR for [NEt_4][*closo*-1-$HCB_{11}H_{11}$], $(CD_3)_2CO$ at 294–299 K, ordered as assignment $\delta(^{11}B)$ (ppm) [$\delta(^1H)$ (ppm)]: BH(12) −6.8 [+2.36], BH(7,8,9,10,11) −13.2 [+1.61] and BH(2,3,4,5,6) −16.3 [+1.45]; additionally $\delta(^1H)$(Et) +3.49 (8H, quartet) and +1.33 (12H, triplet), with $\delta(^1H)$(cluster) +2.81 ppm; $\delta(^{13}C)$(Et) +7.1 and +52.5, and $\delta(^{13}C)$(cluster) +50.9 ppm.

The Cs^+ salts **2a** and **3a** of the known anions $[HCB_{11}H_5Cl_6]^-$ **2** and $[HCB_{11}H_5Br_6]^-$ **3** were thence prepared by the direct halogenation of Cs[$HCB_{11}H_{11}$], essentially according to published procedures.[30] A synthesis of the Cs^+ salt **1a** of the $[1\text{-}HCB_9H_4Br_5]^-$ anion **1** has previously been reported:[31] this was prepared by the direct bromination of the $[1\text{-}HCB_9H_9]^-$ anion under acid conditions. The alternative procedure described as follows is carried out under aqueous alkaline conditions.

Preparation of Cs[*closo*-1-$HCB_9H_4Br_5$] 1a by the direct bromination of Cs[*closo*-1-HCB_9H_9] in alkaline solution. Cs[*closo*-1-HCB_9H_9] (2.0 g, 7.9 mmol) was dissolved in hot aqueous KOH (5%, 50 ml). An excess of elemental Br_2 (*ca.* 8.8 g, 55 mmol) was added dropwise to this solution. The solution was heated at reflux overnight, and then further elemental bromine (*ca.* 2.5 g, 16 mmol) was added and heating at reflux continued. The reaction was monitored by ^{11}B NMR spectroscopy performed on reaction aliquots at intervals to assess for completion. After a further *ca.* 24 h, the reaction was complete. The solution was reduced in volume by *ca.* 50% (rotary evaporator, room temperature, water pump) and the precipitate was filtered off and recrystallised from hot water–ethanol to give Cs[*closo*-1-$HCB_9H_4Br_5$] **1a** in 85% yield as a white crystalline solid. Spectroscopic properties were as reported in the literature.[31]

X-ray crystallography

Crystals were mounted on a glass fibre under oil. Data were collected at 150(2) K on a Bruker SMART diffractometer with silicon-monochromated synchrotron radiation ($\lambda = 0.68830$ Å; UK National SRS facility, Daresbury, station 9.8) for **1a** and on a Nonius KappaCCD diffractometer with graphite-monochromated Mo–Kα radiation ($\lambda = 0.71073$ Å) for **2a** and **3a**. Data were corrected for Lorentz, polarisation and absorption effects. Structures were solved by direct methods using SHELXS-97 and refined with full-matrix least-squares on F^2 using SHELXL-97. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were fully refined for **1a** and included at geometrically estimated positions and refined with a riding model for **2a** and **3a**. One Cs^+ position in **2a** and **3a** showed a symmetry-induced disorder and was modelled at half occupancy. Details of data collections and structure refinements are given in Table 1.†

Table 1 Data collection and details of structure refinements

	1a	2a	3a
Formula	$CH_5B_9Br_5Cs$	$CH_6B_{11}Cl_6Cs$	$CH_6B_{11}Br_6Cs$
M_r	646.80	482.58	749.34
Crystal system	Tetragonal	Monoclinic	Monoclinic
Space group	*P*4/*nmm*	*P*2/*c*	*P*2/*c*
a/Å	8.3873(6)	14.5462(3)	15.0967(3)
b/Å	= *a*	8.8913(2)	9.2460(2)
c/Å	10.5853(12)	12.2784(3)	12.5568(3)
β/°		97.010(1)	97.112(1)
U/Å^3	744.64(11)	1576.15(6)	1739.24(7)
Z	2	4	4
F(000)	572	896	1328
ρ_{calc}/g cm^{-1}	2.885	2.034	2.862
μ/mm^{-1}	15.861	3.334	15.885
Crystal size/mm	0.20, 0.20, 0.04	0.23, 0.13, 0.05	0.17, 0.13, 0.12
$\theta_{min,\ max}$/°	3.00, 26.00	3.08, 26.00	2.59, 26.00
Data collected	3515	23927	18141
Unique data, R_{int}	493, 0.0389	3089, 0.0517	3414, 0.0864
Observed data ($I > 2\sigma(I)$)	481	2849	2976
Parameters	34	177	177
R_1 (obs. data)	0.0613	0.0377	0.0376
wR_2 (all data)	0.1222	0.1018	0.0958
S	1.241	1.086	1.034

Results and discussion

As summarised in the Experimental section above, the Cs^+ salts **2a** and **3a** of the anions $[HCB_{11}H_5Cl_6]^-$ **2** and $[HCB_{11}H_5Br_6]^-$ **3** were prepared by direct halogenation of the $[HCB_{11}H_{11}]^-$ anion according to published procedures,[30] and the Cs^+ salt **1a** of the $[1\text{-}HCB_9H_4Br_5]^-$ anion **1** was prepared by direct bromination of the $[1\text{-}HCB_9H_9]^-$ anion in aqueous alkaline solution. All three anions have been previously reported.[30,31] The starting non-halogenated anions $[1\text{-}HCB_9H_9]^-$ and $[HCB_{11}H_{11}]^-$ were prepared *via* the [*arachno*-6-$H_2CB_9H_{12}]^-$ anion, prepared in turn by the treatment of *nido*-$B_{10}H_{14}$ with HCHO in alkaline solution (eqn. (1)). Oxidative cluster closure of the [*arachno*-6-$H_2CB_9H_{12}]^-$ anion with elemental I_2 in aqueous alkaline solution then effects cluster closure to the [*closo*-2-$HCB_9H_9]^-$ anion (eqn. (2)). The [*closo*-2-$HCB_9H_9]^-$ anion readily isomerises on heating to give the [*closo*-1-$HCB_9H_9]^-$ anion which we were able to isolate as its Cs^+ salt in *ca.* 90% yield.

$$B_{10}H_{14} + HCHO + 2[OH]^- + H_2O \rightarrow [H_2CB_9H_{12}]^- + [B(OH)_4]^- + 2H_2 \quad (1)$$

$$[H_2CB_9H_{12}]^- + 2I_2 + 4[OH]^- \rightarrow [HCB_9H_9]^- + 4I^- + 4H_2O \quad (2)$$

Alternatively, the [*arachno*-6-$H_2CB_9H_{12}]^-$ anion in a cluster-Aufbau reaction with $[BH_3(SMe_2)]$ gave the [*closo*-$HCB_{11}H_{11}]^-$ anion (eqn. (3)), which we were able to isolate as its Cs^+ salt in *ca.* 80% yield. This synthesis mirrors the long-known two-boron insertion reaction that uses $[BH_3(SMe_2)]$ with *nido* ten-vertex $B_{10}H_{14}$ to give the *closo* twelve-vertex $[B_{12}H_{12}]^{2-}$ anion.[32] These two routes represent convenient new entries into these increasingly well studied ten-vertex and twelve-vertex monocarbaborane systems, previous routes being somewhat less convenient as indicated in the Introduction above.

$$2[H_2CB_9H_{12}]^- + 4[BH_3(SMe_2)] \rightarrow 2[HCB_{11}H_{11}]^- + 4SMe_2 + 8H_2 \quad (3)$$

Structure of Cs[1-$HCB_9H_4Br_5$] 1a

The caesium salt **1a** of the $[1\text{-}HCB_9H_4Br_5]^-$ anion **1** crystallises in a tetragonal unit cell and the crystal structure was solved in the space group *P*4/*nmm*. The Cs^+ cation lies on a site of $\bar{4}m2$ symmetry, while the anion lies across the four-fold axis and mirror planes. The structure of the anion is shown in Fig. 1. The molecular structure is similar to that of the previous reports of **1**,[31a] and the fully brominated $[1\text{-}HCB_9Br_9]^-$ anion,[24] and average C–B, B–B and B–Br interatomic distances are

† CCDC reference numbers 248036–248038. See http://www.rsc.org/suppdata/nj/b4/b410929e/ for crystallographic data in .cif or other electronic format.

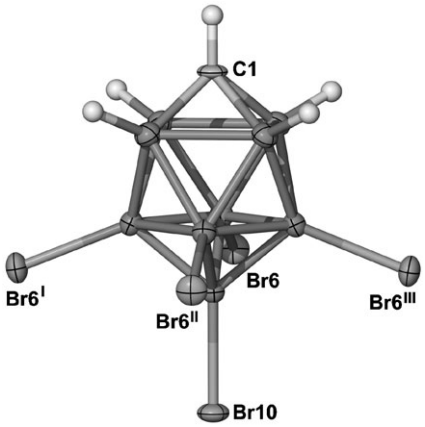


Fig. 1 Crystallographically determined structure of the $[1\text{-}HCB_9H_4Br_5]^-$ anion **1** in its Cs^+ salt **1a**. Ellipsoids are shown at 50% probability levels. Symmetry operations I: $0.5 - y, x, z$; II: $0.5 - x, 0.5 - y, z$; III: $y, 0.5 - x, z$.

unexceptional at 1.600(6), 1.800(6) and 1.949(6) Å, respectively. All interatomic distances are given in Table 2.

$Cs[1\text{-}HCB_9H_4Br_5]$ **1a** is best regarded as an ionic salt, and in the extended crystal structure, $Cs^+\cdots Br$ distances are long at 3.8083(4) and 4.1948(3) Å, noting that the $Cs^+\cdots Br^-$ distance in CsBr itself is *ca.* 3.70 Å.[33] The other Cs^+ salts of halogenated monocarbaborane anions that have been crystallographically investigated are also similarly regarded as ionic salts.[14,18,24,25] The long $Cs\cdots Br$ distances in **1a** are consistent with these previously known structures and are associated with the high coordination number of the Cs^+ cation: this Cs^+ cation is surrounded by four $[HCB_9H_4Br_5]^-$ anions and has a distorted cuboctahedral coordination sphere involving interactions with twelve bromine positions, Fig. 2. A cuboctahedral geometry is unusual for the Cs^+ cation,[34] although it has been reported previously in the solid-state assembly of $Cs[Er_{10}(C_2)_2]I_{18}$, in which the Cs^+ cation is surrounded by twelve iodine atoms, with the $Cs\cdots I$ distances ranging from 3.93 to 4.31 Å.[35] A similar coordination sphere is also observed in $CsAsF_6$.[36] Otherwise, twelve-coordinate Cs^+ complexes generally involve macrocyclic ligands or assemblies where the metal geometry is dictated by the macrocycle rather than by less concerted individual interactions.[37]

The extended structure of **1a** is demonstrated by the lattice fragments shown in Fig. 3. Each Cs^+ cation interacts with four

Table 2 Selected interatomic distances (Å)

Complex 1a			
Cs(1)–Br(6)	3.8083(4)	B(6)–B(10)	1.690(6)
Cs(1)–Br(10)	4.1948(3)	B(6)–B(6)^{I}	1.840(6)
C(1)–B(2)	1.600(6)	B(6)–Br(6)	1.963(4)
B(2)–B(6)	1.816(5)	B(10)–Br(10)	1.935(8)
B(2)–B(2)^{I}	1.857(6)		

Complex 2a			
Cs(1)–Cl(9)	3.8372(11)^{IV}	B(2)–B(6)	1.782(6)
Cs(1)–Cl(10)	3.9949(11)	B(3)–B(8)	1.770(6)
Cs(1)–Cl(10)	4.0238(10)^{V}	B(10)–B(11)	1.788(6)
Cs(1)–Cl(11)	4.0455(11)^{VI}	Cl(7)–B(7)	1.800(4)
Cs(1)–Cl(12)	3.6815(9)^{VII}	Cl(8)–B(8)	1.798(4)
C(1)–B(4)	1.693(6)	Cl(9)–B(9)	1.798(4)
C(1)–B(3)	1.696(6)	Cl(10)–B(10)	1.797(4)
C(1)–B(5)	1.708(6)	Cl(11)–B(11)	1.791(4)
B(2)–B(7)	1.775(6)	Cl(12)–B(12)	1.794(4)
B(2)–B(8)	1.779(6)		

Symmetry operations: I: $-y + 0.5, x, z$; IV: $2 - x, y, z + 0.5$; V: $x, -y, z - 05$; VI: $x, y - 1, z$; VII: $2 - x, -y, 1 - z$.

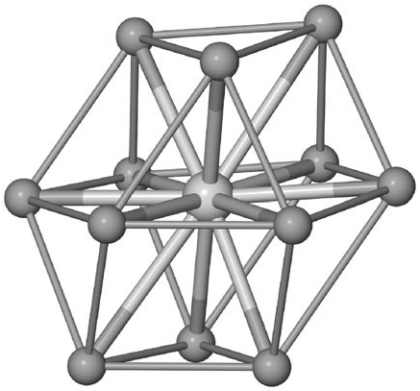


Fig. 2 The irregular cuboctahedral coordination geometry of the Cs^+ cation in the $[1\text{-}HCB_9H_4Br_5]^-$ salt **1a**.

$[HCB_9H_4Br_5]^-$ anions and each anion interacts with four Cs^+ cations forming a two-dimensional (2D) grid structure with (4,4) topology. By contrast, the other crystallographically investigated Cs^+ salt of a brominated $\{CB_9\}$ monocarbaborane, $Cs[HCB_9Br_9]$, forms a quasi-1D chain structure.[24] In **1a** there are two types of bromine atom that interact with the Cs^+ cation. The apical bromine atom *para* to the monocarbaborane C–H group exhibits interactions with four Cs^+ cation sites in a square plane, whereas the *meta* bromine sites bridge between two Cs^+ cations in a bent arrangement, with $Cs^+\cdots Br\cdots Cs^+$ angles of 102.275(16)°. The Cs^+ cations and the *para* bromine units are nearly coplanar within the 2D grid, with the $Cs^+\cdots Br\cdots Cs^+$ angle at 177.29(2)°, and the bulk of the monocarbaborane cages is positioned above or below this plane. The 2D extended grids pack together in the crystal

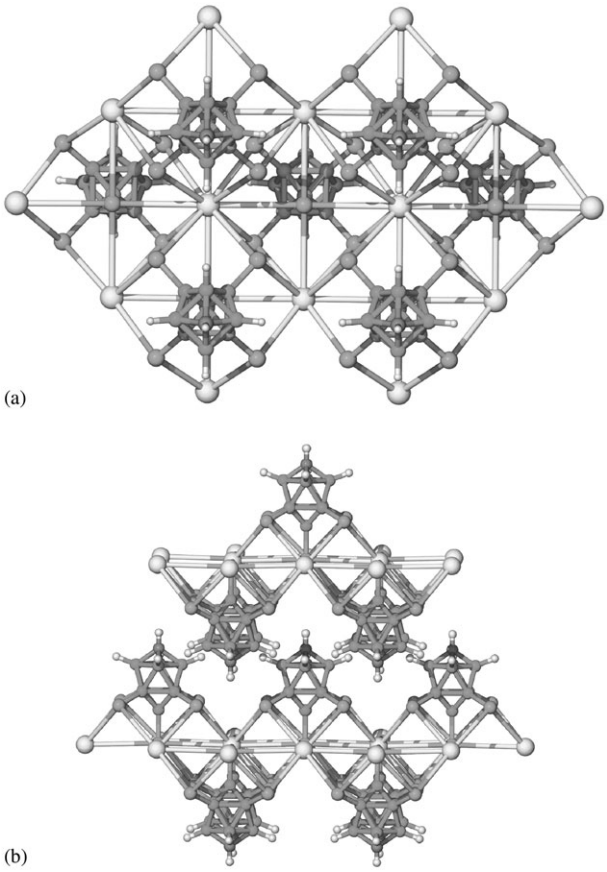


Fig. 3 Fragments of the extended structure of $Cs[1\text{-}HCB_9H_4Br_5]$ **1a** showing (a) the 2D grid of (4,4) topology, viewed along the perpendicular to the crystallographic *ac* plane and (b) the packing of such grids, viewed parallel to the *bc* plane.

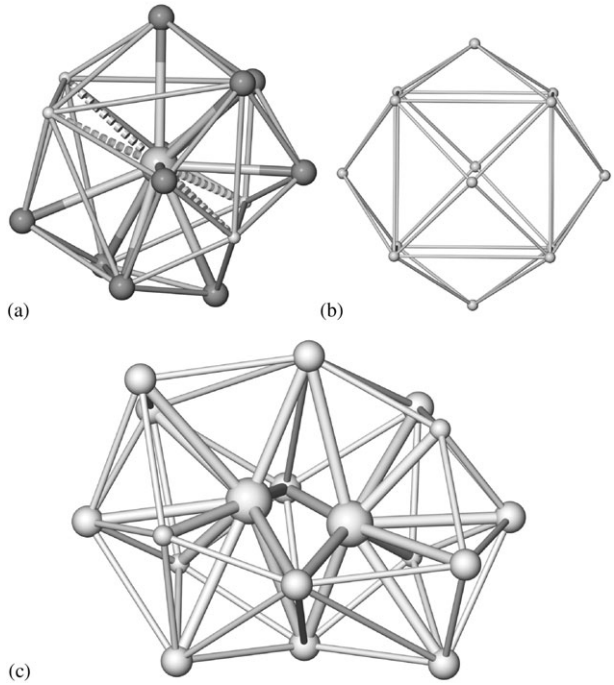


Fig. 4 Coordination geometries of the Cs^+ cations in $Cs[HCB_{11}H_5Cl_6]$ **2a**: (a) the irregular tetrakis hexahedral geometry about Cs(1) with the longer Cs···H contacts shown as hatched lines; (b) an idealised tetrakis hexahedron; and (c) the coordination of a pair of disordered Cs(2) positions by chlorine and hydrogen atoms from the anionic units.

lattice to form an overall 3D layered structure, with double layers of monocarbaborane anions separated by the coplanar $Cs^+\cdots Br$ layers [Fig. 3(b)]. Closest contacts between the grids are non-polar, between B–H groups, with a B–H···H–B inter-hydrogen distance of 2.547 Å. The C–H hydrogen atom of each $[HCB_9H_4Br_5]^-$ anion is 3.314 Å away from four symmetry-equivalent bromine sites on an adjacent 2D grid.

Structure of $Cs[HCB_{11}H_5Cl_6]$ 2a and $Cs[HCB_{11}H_5Br_6]$ 3a

The Cs^+ salt **2a** of the $[HCB_{11}H_5Cl_6]^-$ anion **2** crystallises in a monoclinic cell and the structure was solved in the space group $P2/c$. The structure of the analogous bromo compound $Cs[HCB_{11}H_5Br_6]$ **3a** is isostructural with **2a**; hence only **2a** is discussed in detail. The asymmetric unit of **2a** consists of one $[HCB_{11}H_5Cl_6]^-$ anion and two half-occupied Cs^+ sites. One Cs^+ cation resides on a two-fold axis, whereas the other is on a general position, although disordered across the two-fold axis. The molecular structure of the individual $[HCB_{11}H_5Cl_6]^-$ anion **2** has been previously reported,[7] and that of **3** has been reported as part of a complex.[20] The molecular structures of these two anions within **2a** and **3a** are consistent with these other reports, selected interatomic distances are given in Table 2 for **2a**.

The overall crystal structure of **2a** is complicated. As for **1a**, the 'long' $Cs^+\cdots Cl–B$ interatomic distances indicate that **2a** is best regarded as an ionic solid. The two crystallographically distinct types of Cs^+ cation, however, show very different coordination behaviour.

The cation at position Cs(1), which is located on a two-fold axis, is surrounded by six $[HCB_{11}H_5Cl_6]^-$ anions. There are ten B–Cl···Cs^+ interactions, at distances ranging from 3.6815(9) to 4.0455(11) Å in an irregular geometry (Table 2). This gives a coordination shell that at first sight appears to be incomplete, as a circumscribing ten-vertex geometry would entail an open face. However, there are closest secondary interactions from four B–H groups within 4 Å of Cs(1), at B–H···Cs distances of 3.453 and 3.669 Å. Overall, the ten B–Br positions and the four secondary B–H positions define a fourteen-vertex polyhedron around the Cs(1) position, as shown in Fig. 4(a). This polyhedron has a distorted tetrakis hexahedral structure. The tetrakis hexahedron is essentially a hexa-capped cube and the idealised structure of cubic symmetry for this is shown in Fig. 4(b): to the best of our knowledge, this coordination geometry in structural chemistry has previously only been presented on a theoretical basis.[38] In summary, the coordination shell of Cs(1) may be regarded as either (a) an irregular and open ten-vertex coordination sphere or (b) a distorted tetrakis hexahedron with four long contacts.

The other type of Cs^+ cation centre, Cs(2), is disordered over two positions 2.33 Å apart across a two-fold axis, with each Cs(2) site having 50% occupancy. Such disorder renders it difficult to define exact coordination geometries. Each pair of disordered Cs(2) positions is coordinated by six $[CB_{11}H_6Cl_6]^-$ anions, involving twelve B–Cl···Cs^+ interactions at interatomic distances ranging from 3.5709(11) to 3.9833(12) Å, and involving four B–H···Cs^+ contacts at 3.043 Å. The coordinating chlorine and hydrogen atoms form a cage reminiscent of two mutually fused icosahedral fragments [see Fig. 4(c)].

The packing diagram for **2a** is shown in Fig. 5 with the Cs(1) positions shown as large light spheres and the disordered Cs(2) positions as dark spheres. The overall structure is a 3D lattice. Each monocarbaborane anion in **2a** is equivalent, and each interacts with three Cs(1) cations and three pairs of disordered Cs(2) cations, whereas each metal cation site and each disordered cation pair interacts with six anions.

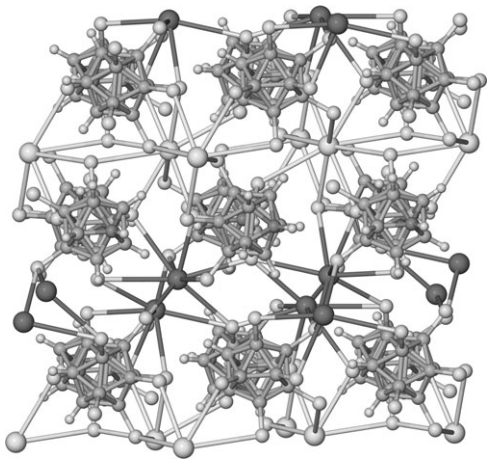


Fig. 5 Packing diagram of the crystal structure of **2a** illustrating the 3D lattice formed by bridging anions and Cs^+ centres. The Cs(1) positions are shown as light spheres and the Cs(2) positions as dark spheres. Note that each Cs(2) position has 50% occupancy due to a symmetry-imposed disorder.

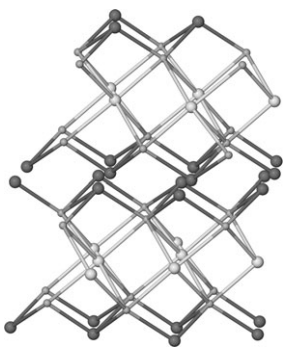


Fig. 6 Connectivity diagram of the crystal structure of **2a** (compare Fig. 5) illustrating how the ionic components form a layered 3-D structure. Large light spheres are Cs(1), dark spheres are disordered Cs(2) positions, and small spheres are the centres of the $[HCB_{11}H_5Cl_6]^-$ anions. The apparent break in the structure is an artefact of disorder (see text).

The structure is layered, with planes of cations and anions alternating in the crystallographic *a* direction with a Cs(1)···anion···Cs(2)···anion···Cs(1) repeating chain motif. A simplified connectivity diagram is shown in Fig. 6, in which the centre of each monocarbaborane anion is shown as a small sphere. The apparent break in the structure is an artefact of the disorder of Cs(2).

Conclusion

The crystal structures of $Cs[1\text{-}HCB_9H_4Br_5]$ **1a** and $Cs[HCB_{11}H_5X_6]$ (X = Cl **2a**, Br **3a**) show long interatomic distances between the cationic and anionic components. Interactions between the ionic components occur through B–X···Cs and B–H···Cs contacts, behaviour consistent with previously characterised Cs^+ salts of halogenated monocarbaborane anions. The coordination numbers of the Cs^+ cations within the lattices of **1a**, **2a** and **3a** are, however, high, with an unusual twelve-coordinate cuboctahedral coordination sphere for **1a**, and with non-regular fourteen-vertex coordination geometries for mutually isostructural **2a** and **3a**. In the structures of the latter two species, the Cs(1) centre can be considered to have a distorted tetrakis hexahedral geometry involving four secondary B–H···Cs interactions as well as ten primary B–Cl···Cs contacts (compound **2a**) or B–Br···Cs contacts (compound **3a**). The overall 3D assemblies of **1a** on one hand, and of **2a** and **3a** on the other, are structurally quite distinct. In **1a** the smaller anions **1** form a 2D sheet structure with the Cs^+ cations; these sheets then pack in layers to form the 3D macrostructure with no significant cation–anion interaction between successive sheets, and the Cs^+ atom positions are well defined. On the other hand, in **2a** and **3a** the interionic interactions between the Cs^+ cations and the anions directly engender a 3D interionic lattice, and there is some disordering of cation sites also.

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