doi.org/10.1002/hlca.202200163

RESEARCH ARTICLE

HELVETICA chimica acta

Halocyclopropenium-Halide Halogen-Bonded Ion Pairs and Their Hydrogen-Bonded Halide Solvates

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A series of salts with a diaminohalocyclopropenium cation and halide anion $[C_3(N^iPr_2)_2X]X$ (X = Cl ([**1**]Cl) or Br ([**2**]Br) were isolated with a variety of solvates and, in one case, as a co-crystal with hydronium chloride. In particular, the initial synthesis of [**1**]Cl formed a co-crystal with hydronium and with CH_2Cl_2 solvate ($[\mathbf{1}]_2[OH_3Cl_3]\cdot CH_2Cl_2$) upon isolation from acetone/CH_2Cl_2. Recrystallization of this from chloroform gave a dichloroform adduct $[\mathbf{1}]Cl\cdot 2CHCl_3$, whereas treatment with ICl formed an octahalide cluster $[\mathbf{1}]_2I_4Cl_4$. The bromine salt $[\mathbf{2}]Br\cdot C_2H_4Br_2$ was prepared by treatment of [**1**]Cl with dibromoethane and was isolated as a solvate. The hydronium cation was found as part of a hydronium trichloride cluster $[OH_3Cl_3]^{2-}$ and this, along with a partially-deuterated analogue of $[OHD_2Cl_3]^{2-}$ and $[OD_3Cl_3]^{2-}$, was studied computationally and by mid- and far-infrared spectroscopy. Significant halogen bonds were found between $\mathbf{1}^+$ or $\mathbf{2}^+$ and chloride or bromide, respectively. On the other hand, the distance to the octahalide $[I_4Cl_4]^{2-}$ is too long for a halogen bond. Hydrogen bonding from the halides to the halomethane solvates is also significantly stronger than to the cation isopropyl groups. The geometries formed at the halide ions with respect to the halogen bond and strong hydrogen bonds are pyramidal with approximately orthogonal angles.

Keywords: halides, halogens, halogen bonding, hydrogen bonds, X-ray diffraction.

Introduction

Halogen bonding can result when a halogen atom forms a σ bond, R–X; a region of positive charge (a σ hole) will then form on the halogen opposite the σ bond and this halogen bond donor atom can then form an electrostatic interaction with a lone pair, or region of negative charge, from some other atom, the halogen bond acceptor.[1–4] HOMO–LUMO interactions are also important, in addition to some contribution from dispersive forces.[3,5,6] The magnitude of this σ hole increases down the halogen group and is thus most significant for bromine and iodine. It also increases with increasing electronegativity of the group attached to the halogen, for example, N–Cl *versus* C–Cl.[7–11] It should also be noted that there is a region of negative charge in a ring around the halogen and orthogonal to the σ hole, thus the halogen atom can potentially act as both a halogen-bond donor and halogen-bond acceptor. In the case of the polyhalides, this frequently results in combinations of linear and orthogonal bond angles, such as is found in the Z-shaped octahalides X_8^{2-} (X = Br, I).[12–14] Halogen bond donor strengths can be increased by use of halogenated cations, particularly of brominated and iodinated imidazolium compounds.[15,16] Notably, *Holthoff et al.* have also reported 'anti-electrostatic' halogen bonding, in which the halogen bond donor and acceptor have the same non-zero charge, between the iodinated bis(dicyanomethylene)cyclopropanid derivative $[C_3(C(CN)_2)_2I]^-$ and I^-.[17] The halogen bond donor ability of organo-

Supporting information for this article is available on the WWW under https://doi.org/10.1002/hlca.202200163

chlorides, however, is significantly less than that of analogous bromides and iodides. *Kukushkin* and co-workers found that the maximum electrostatic potential on Cl in CH_2Cl_2 is about one tenth that of I in CH_2I_2, Cl in $CHCl_3$ is about one third that of I in CHI_3 and Cl in CCl_4 is about half that of I in CI_4.[18] Consequently, despite CH_2Cl_2 and $CHCl_3$ ranking as second- and fifth-most common solvents, respectively, in crystal structures, the number of observed halogen bonds with these molecules is relatively small.[18,19] The chloride anion on the other hand is potentially a good halogen-bond acceptor; however, its interactions tend to be dominated by its preference for hydrogen bonding, so the number of halogen bonds with chloride is limited. The chloride–water hydrogen bond, for example, is significantly stronger than the water–water hydrogen bond.[20] Similarly, chloroalkanes such as CH_2Cl_2 and $CHCl_3$ much prefer to form hydrogen bonds to chloride than halogen bonds.[21] Indeed, hydrogen bonding to chloride is of particular interest for its role in biological systems, where it is prolific, as well as its applications in asymmetric catalysis and in anion receptors.[22–28] A search of the Cambridge Structural Database (CSD) by *Awwadi et al.* in 2007 found just 13 C–Cl···Cl^- halogen bonding examples.[29]

In the work reported here, we will describe the halogen bond donor ability of halogen-substituted (both Cl and Br) diaminocyclopropenium cations to halide ions (Cl^- and Br^-) along with hydrogen bonds to these halide ions, including a rare example of a hydronium trichloride cluster.

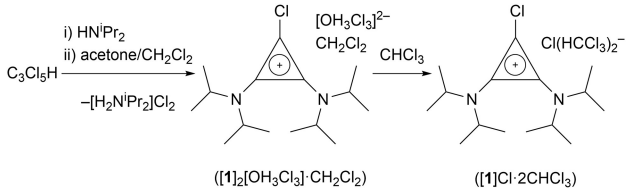
Results and Discussion

Synthesis

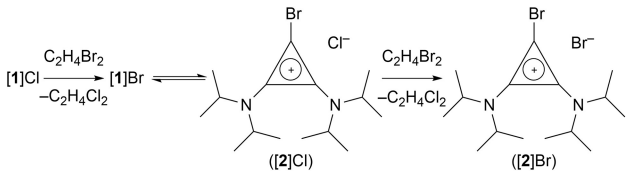
$[C_3(N^iPr_2)_2Cl]Cl$ ([**1**]Cl) has been known since work on triaminocyclopropenium (TAC) salts began in the 1970s.[19] It was found then that bulky secondary amines such as HN^iPr_2 would not form a triaminocyclopropenium cation (although we later showed that it can form) but would instead lead to a diaminochlorocyclopropenium cation ($\mathbf{1}^+$). The cation was initially isolated as the perchlorate salt [**1**]ClO_4 by *Yoshida* and *Tawara*.[30,31] *Weiss* and coworkers reported some early studies on its use in a variety of transformations, including the preparation of a cyclopropenylidene complex.[32–35] Amongst its more recent uses, *Bertrand* has used it to isolate cyclopropenylidenes[36] and Lambert as a 'ClickablL' reagent to prepare poly(ionic liquids).[37] Although it has been used frequently, reports on its isolation or properties are scarce and references to its synthesis frustratingly lead back to *Yoshida* and *Tawara*'s initial report of the perchlorate salt, rather than the chloride salt. *Taylor* reported NMR and crystallographic data for the perchlorate salt.[38,39] We initially attempted to isolate [**1**]Cl by addition of acetone to remove $[^iPr_2NH_2]Cl$ by precipitation followed by crystallization from CH_2Cl_2 (*Scheme 1*). However, this was found to co-crystallize with hydronium chloride (generated from water in the undried acetone and H^+ from the ammonium salt side product) and CH_2Cl_2 solvate as $[\mathbf{1}]_2[OH_3Cl_3]\cdot CH_2Cl_2$. Crystallization of this from a chloroform solution was found to give the dichloroform solvate $[\mathbf{1}]Cl\cdot 2CHCl_3$. The solid-state structures of both $[\mathbf{1}]_2[OH_3Cl_3]\cdot CH_2Cl_2$ and $[\mathbf{1}]Cl\cdot 2CHCl_3$, as discussed in detail below, were found to have a halogen bond between the chloro substituent on the cation and a chloride anion.

Previously, we have converted TAC chloride salts to bromide or iodide salts by heating them to reflux in a solution of an alkyl halide, such as dibromoethane or iodoethane, respectively.[40] When we similarly treated [**1**]Cl with dibromoethane, we found that not only was the chloride replaced by bromide, but the chloro substituent was also replaced by bromine to give $[C_3(N^iPr_2)_2Br]Br$ ([**2**]Br; *Scheme 2*). This salt was then isolated as the dibromoethane solvate $[\mathbf{2}]Br\cdot C_2H_4Br_2$ and found to have bromo-bromide halogen bonding.

As part of our studies on polyhalides,[41–44] we treated $[\mathbf{1}]_2[OH_3Cl_3]$ with two equivalents of ICl under reflux in CH_2Cl_2. We were hoping that the C_{2v}-symmetric cation would favor the crystallization of a



Scheme 1. Syntheses of $[C_3(N^iPr_2)_2Cl]Cl$ co-crystallized with hydronium chloride and CH_2Cl_2 solvate or crystallized with $CHCl_3$ solvate.

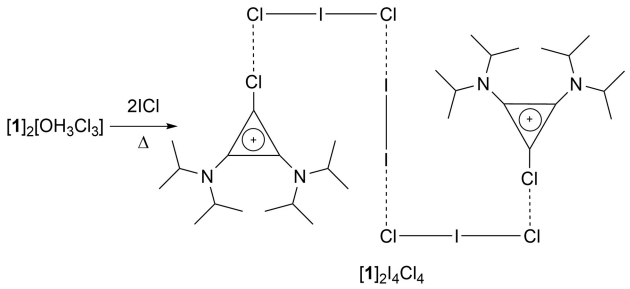


Scheme 2. Proposed route for the synthesis of the bromo-bromide salt $[C_3(N^iPr_2)_2Br]Br$ ([**2**]Br).

C_{2v}-symmetric pentahalide $I_2Cl_3^-$. Instead, it was found to give the octahalide-containing salt $[C_3(N^iPr_2)_2Cl][I_4Cl_4]$ ($[\mathbf{1}]_2I_4Cl_4$) which possibly exhibits very weak halogen bonding between the cation and the anion (*Scheme 3*). We recently reported a series of iodine-chlorine octahalides, including $[C_3(NEt_2)_3]_2[I_4Cl_4]$ which was prepared by treatment of $[C_3(NEt_2)_3]ICl_2$ with I_2.[41] The formation of the central I_2 in $[\mathbf{1}]_2I_4Cl_4$ is due to halogen-redistribution reactions.

Solid State Structures

$[C_3(N^iPr_2)_2Cl]_2[OH_3Cl_3]\cdot CH_2Cl_2$ crystallizes in the monoclinic space group $P2_1/c$. The asymmetric unit contains two cations of $\mathbf{1}^+$, a hydronium cation, three chlorides and one CH_2Cl_2 solvate molecule. *Figure 1* illustrates the atomic labeling scheme and asymmetric unit. The presence of an electronegative and weak π donor Cl ring substituent in the cation leads to a change in the C_3 ring bond distances in which C1–C3 and C2–C3 are slightly shortened (1.360(3)–1.366(3) Å) compared to symmetrical TAC cations at *ca.* 1.38 Å,[45] but similar to those in $[C_3Cl_3][AlCl_4]$ which average 1.356 Å.[46] C1–C2, however, is elongated compared to symmetric TAC cations (1.432(3) Å and 1.429(3) Å). This variation in the bond distances can be attributed to increased π donation into the C_3 ring from the planar diisopropylamino groups (the sum of the angles around N1 and N2 are >359°). The C–Cl distances for the two independent cations are essentially the same (1.690(2) and 1.688(2) Å for C3–Cl5 and C3 A–Cl6, resp.) and are shorter than in the CH_2Cl_2 solvate (1.762(3) and 1.785(2) Å), but longer than in $[C_3Cl_3][AlCl_4]$ (mean = 1.631 Å) which implies reduced π donation from the chloro atom in $\mathbf{1}^+$.[46] Each cation of $\mathbf{1}^+$ uses a σ hole on the chloro substituent to form a weak halogen bond to a chloride. The two halogen bonding Cl^-–Cl distances are very different, 3.2718(6) Å for Cl1–Cl5 and 3.7359(7) Å for Cl2–Cl6, but are both close to having linear C–Cl–Cl angles (177.59(8)° and 171.40(7)°, resp.). Halogen-bonding parameters for the compounds described in this article are collected in *Table 1*. A ratio (R_D) of the interatomic distance and the sum of the atomic and ionic radii is a useful measure of the strength of the halogen bond, with an R_D of greater than one implying that there is no halogen bond. Cl has an atomic radius of 1.75 Å whereas the chloride ion has an ionic radius of 1.81 Å,[47,48] and on this basis the long Cl2–Cl6 distance would not be considered a halogen bond whereas the shorter Cl1–Cl5 distance would be. These distances can be compared to the longer anti-electrostatic Cl–Cl



Scheme 3. Synthesis of the octahalide-containing salt $[C_3(N^iPr_2)_2Cl]_2I_4Cl_4$ ($[\mathbf{1}]_2I_4Cl_4$).

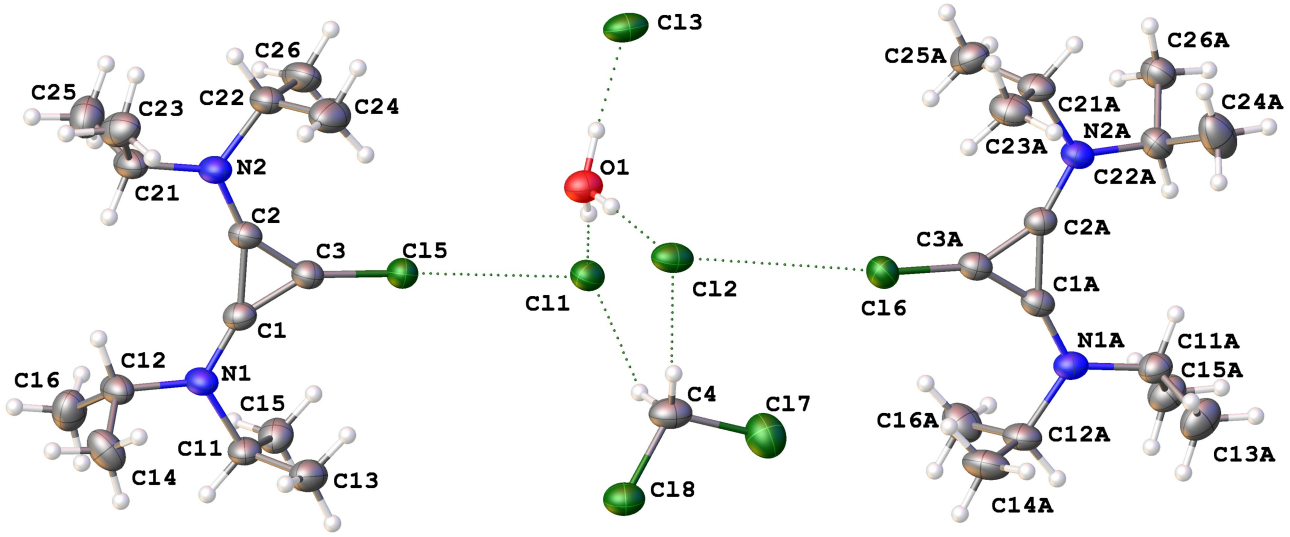


Figure 1. Thermal ellipsoid plot of $[\mathbf{1}]_2[OH_3Cl_3]\cdot CH_2Cl_2$ illustrating the asymmetric unit and the atomic-labelling scheme.

Table 1. Halogen-bonding parameters.

C–Cl	Distance [Å]	Cl–Cl	Distance [Å]	R_D[a]	C–Cl–Cl	Angle [°]
[**1**]$_2$[OH_3Cl_3]·CH_2Cl_2						
C3–Cl5	1.690(2)	Cl1–Cl5	3.2718(6)	0.919	C3–Cl5–Cl1	177.59(8)
C3 A–Cl6	1.688(2)	Cl2–Cl6	3.7359(7)[b]	1.049	C3 A–Cl6–Cl2	171.40(7)
[**1**]Cl·2$CHCl_3$						
C1–Cl0	1.673(4)	Cl1–Cl0	3.1290(13)	0.879	C1–Cl0–Cl1	168.39(13)
C1 A–Cl0 A	1.675(4)	Cl2–Cl0 A	3.2514(12)	0.913	C1 A–Cl0 A–Cl2	170.40(12)
C1B–Cl0B	1.677(4)	Cl3–Cl0B	3.2602(11)	0.916	C1B–Cl0B–Cl3	171.09913)
[**2**]Br.$C_2H_4Br_2$						
C3–Br2	1.852(4)	Br1–Br2	3.2242(6)	0.846	C3–Br2–Br3	173.93(12)
[**1**]$_2I_4Cl_4$						
C3–Cl3	1.693(6)	Cl2–Cl3	3.952(3)[b]	1.110	C–Cl3–Cl2	171.4(2)

[a] Ratio of X–X distance and sum of the *van der Waals* and ionic radii. [b] Distance is too long to normally be considered a halogen bond.

halogen bond distances formed between ICl_2^- and $I_2Cl_3^-$ of 3.497 Å (R_D = 0.982) and $BrCl_2^-$ and $Br_2Cl_3^-$ of 3.359 Å (R_D = 0.944).[41,42] In those cases, the σ hole on the chlorine atom is formed by the attached electronegative halogen, whereas, in the case of $\mathbf{1}^+$, it is formed by the electron-withdrawing effects of the attached cyclopropenium cation. Also of relevance are the organochloro chloride salts 2-chloropyridinium chloride (Cl···Cl^- = 3.507, R_D = 0.985),[49] 3-chloropyridinium chloride (Cl···Cl^- = 3.479, R_D = 0.977),[49] 4-chloropyridinium chloride (Cl···Cl^- = 3.3352, R_D = 0.937),[50] and 1,3-dimethyl-4,5-dichloroimidazolium chloride in which the chloride has two halogen bonds, at 3.2688(8) and 3.2232(8) Å, R_D = 0.918 and 0.905, respectively.[51] The R_D values for the latter imidazolium salt are most similar to that of the chloride salts described here. Presumably, the longer of the two Cl^-—Cl distances in [**1**]$_2$[OH_3Cl_3] is caused by crystal-packing effects (a weak halogen bond would be expected to have a relatively wide and shallow potential well and thus be easily compressed or elongated/broken), and the shorter distance is probably a more accurate reflection of the potential halogen-bonding strength between a chloro-TAC cation and a chloride. Intriguingly, *Kukushkin* and coworkers reported a series of CH_2Cl_2 solvates of chloride salts in which most formed CH–Cl^- hydrogen bonds, however, two formed a CCl–Cl^- halogen bond with Cl–Cl distances of 3.276(3) Å (R_D = 0.920) and 3.236(2) Å (R_D = 0.909).[18] The authors suggested that the halogen-bond formation, rather than hydrogen-bond formation, was due to crystal-packing constraints. They also identified nine similar structures in the CCDC database with Cl–Cl distances in the range 3.26–3.50 Å. For Cl–Cl halogen bonds between neutral molecules, *Allen* found 63 structures with CH_2Cl_2–Cl–C halogen bonds in the Cambridge Structural Database (CSD).[19] The Cl–Cl distances range 3.03–3.50 Å with a mean of 3.39 Å (R_D = 0.969). Similarly, for $HCCl_3$–Cl–C halogen bonds, they found 134 examples with a range of 2.62–3.50 Å and a mean of 3.38 Å (R_D = 0.966). On that basis, the CCl^+–Cl^- halogen bonds with $\mathbf{1}^+$ appear to be only slighter shorter than typical CCl–Cl^- halogen bonds for neutral molecules.

As well as the halogen bonds, these chlorides are also bridged through hydrogen bonding to the hydronium cation and the CH_2Cl_2 solvate. As would be expected, the hydrogen bonds to the hydronium (Cl^-–H = 2.0760(5) and 2.0746(5) Å) are significantly stronger/shorter than the hydrogen bonds to CH_2Cl_2 (Cl^-–H = 2.7264(5) and 2.5584(5) Å). The hydrogen-bonding parameters are given in *Table 2*. *Allen* found

Table 2. Hydrogen-bonding parameters for [**1**]$_2$[OH_3Cl_3]·CH_2Cl_2.

Hydrogen bond (D–H–A)	D–H [Å]	H–A [Å]	D–A [Å]	D–H–A [Å]
O1-H1a–Cl1	0.8500(17)	2.0760(5)	2.9215(17)	173.01(11)
O1-H1b–Cl2	0.8498(17)	2.0746(5)	2.9232(18)	176.46(12)
O1-H1c–Cl3	0.99(4)	1.87(4)	2.8619(18)	176(3)
C4-H4b–Cl2	0.970(2)	2.5584(5)	3.523(2)	172.80(14)
C4-H4a–Cl1	0.970(2)	2.7264(5)	3.623(3)	153.94(14)

53 structures with CCl_2H_2–Cl^- hydrogen bonds in the CSD.[19] The H–Cl distances ranged from 2.33–2.95 Å with a mean of 2.57 Å.

Another notable feature of the halogen-bonded chloride ions is their pyramidal geometries; the Cl–Cl–H angles being either very acute (77.222(16)° and 76.652(15)°) or nearer 100° (99.598(17)° and 107.91(2)°) while the H–Cl–H angles are both acute (81.488(16)° and 81.444(18)°). This is in fact a common feature of chloride geometries involving weak bonds,[52] as we will also see in the other salts described here.

The third chloride ion in the asymmetric unit, Cl3, has only one strong hydrogen bond, which is to the hydronium cation. The Cl–O distance is consequently shorter than to the other two chlorides (2.8619(18) Å *versus* 2.9215(17) Å and 2.9232(18) Å) and so the Cl^-–H distance is shorter (1.87(4) Å) and the O–H distance longer (0.99(4) Å *versus* 0.850(2) Å). In terms of the weaker CH–Cl^- hydrogen bonds to the cations, Cl3 has four Cl^-–H distances in the range 2.70–2.90 Å whereas Cl1 and Cl2 have only one each.

The hydronium cation has the expected trigonal pyramidal geometry and, with the three hydrogen-bound chloride ions, forms an $[OH_3Cl_3]^{2-}$ cluster. The Cl–O–Cl angles are near tetrahedral (Cl1–O1–Cl2 = 114.27(5)°; Cl1–O1–Cl3 = 108.31(6)°; Cl2–O1–Cl3 = 114.38(6)°; sum = 337.0°). Whereas there are many reports of crystallographically-characterized hydronium salts (see references [37–40] for some examples), we know of only two other discrete structures of hydronium trichloride $[OH_3Cl_3]^{2-}$. *Willey* and co-workers synthesized $[GeCl_3(L^1)]_2[H_3O]Cl_3 \cdot MeCN$, where L^1 is 1,4,7-trimethyl-1,4,7-triazacyclononane.[53] The Cl–O distances are 2.852(2), 2.860(2) and 2.888(2) Å and the Cl–O–Cl angles are 112.53(8)°, 111.93(8)° and 107.12(7)° (sum = 331.6°). In 2011, *Denton* and co-workers reported an alkoxyphosphonium chloride in which a discrete hydronium trichloride cluster was co-crystallized.[54] The Cl–O distances are 2.855(2), 2.871(2) and 2.892(2) Å and the Cl–O–Cl angles are 108.73(7), 106.69(6) and 126.73(7)° (sum = 342.2°). Thus, it can be seen that our structure has two Cl–O distances that are longer than all of the others, and this can probably be attributed to the additional halogen bonding to those chlorides.

The salt $[C_3(N^iPr_2)_2Cl]Cl \cdot 2CHCl_3$ ([**1**]Cl·2$CHCl_3$) crystallizes in the orthorhombic space group $P2_12_12_1$, and the asymmetric unit shows three independent clusters of [**1**]Cl·2$CHCl_3$. The most notable feature of these clusters is the strong halogen bonding between the chloride and the chloro substituent of the cations (*Figure 2*); the Cl^-–Cl distances are 3.1290(13), 3.2514(12) and 3.2602(11) Å (*Table 1*). Again, the C–Cl–Cl angles are approximately linear (168–171°). These Cl–Cl distances are all shorter, and have smaller R_D values, than the halogen bonds in $[\mathbf{1}]_2[OH_3Cl_3] \cdot CH_2Cl_2$ and this may be attributed to the much weaker hydrogen bonds of the chloride to the chloroform solvate, compared to the hydronium. There is essentially no effect on the structural features of the cation compared to the cations in $[\mathbf{1}]_2[OH_3Cl_3] \cdot CH_2Cl_2$, with the C–Cl distances ranging from 1.673(4) to 1.677(4) Å. The chloride-chloroform Cl–H hydrogen bond distances (*Table 3*) lie in the range of 2.33–2.47 Å (mean = 2.41 Å) which is shorter than in

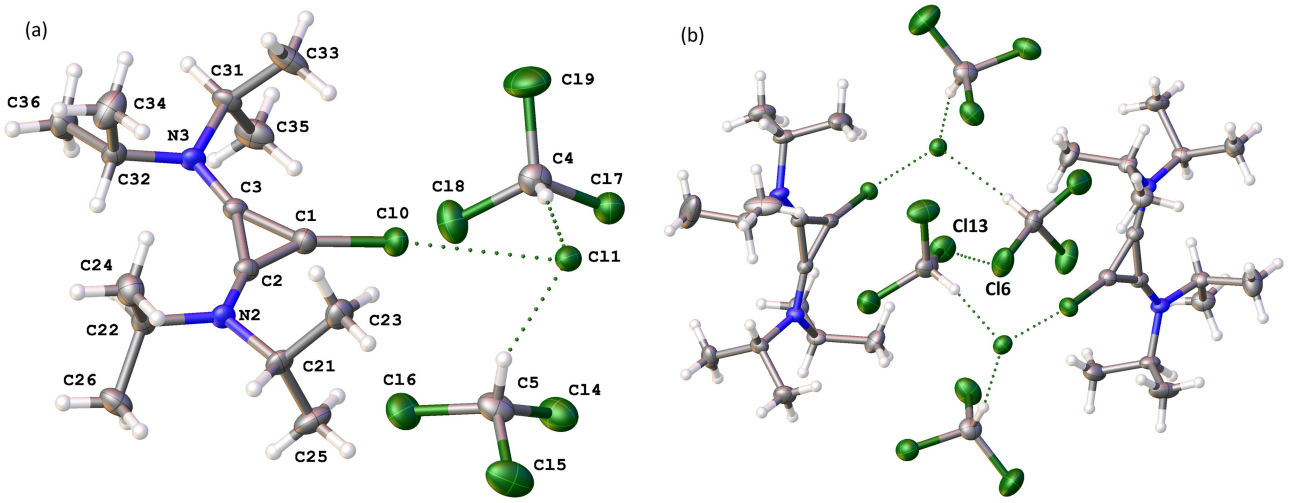


Figure 2. (a) Thermal ellipsoid plot of [**1**]Cl·2$CHCl_3$ illustrating one of three similar clusters in the asymmetric unit (see *Supporting Information*); (b) Illustration of the chloroform–chloroform interaction between Cl6 and Cl13.

Table 3. Hydrogen-bonding parameters for [**1**]Cl·2CHCl$_3$.

Hydrogen bond (D–H–A)	D–H [Å]	H–A [Å]	D–A [Å]	D–H–A [°]
C4–H4–Cl1	0.980(4)	2.3784(9)	3.347(4)	169.6(2)
C5–H5–Cl1	0.980(4)	2.4671(9)	3.401(4)	159.3(3)
C6–H6–Cl2	0.981(4)	2.4399(9)	3.417(4)	174.5(2)
C7–H7–Cl2	0.980(4)	2.3824(9)	3.336(4)	164.3(3)
C8–H8–Cl3	0.980(4)	2.3379(7)	3.306(4)	169.5(3)
C9–H9–Cl3	0.981(4)	2.4676(7)	3.430(4)	166.9(3)

[**1**]$_2$[OH_3Cl_3]·CH_2Cl_2, probably due to a combination of chloroform being a better hydrogen-bond donor and the lack of a competing chloride-hydronium hydrogen bond making the chloride a better hydrogen-bond acceptor. Allen found 38 examples of chloroform-chloride hydrogen bonding, with H–Cl = 2.26–2.80 Å and also with a mean of 2.41 Å.[19] The chlorides also have some weaker hydrogen bonds to isopropyl groups (Cl–H distances of 2.80–2.85 Å).

Additionally, as seen in *Figure 2,b*, there is a halogen bond between two chloroform molecules (Cl6–Cl13); this has a Cl–Cl distance of 3.3443(19) Å (R_D = 0.956).[55] As noted above, *Allen* found a mean distance of 3.38 Å for related halogen bonds with chloroform molecules.[19] *Kukushkin* similarly reported Cl–Cl halogen bonds between chloride-chloroform clusters, with Cl–Cl distances of 3.35–3.54 Å.[21] Notably, the chloroform-chloroform halogen bonds in [**1**]Cl·2CHCl$_3$ are not as linear (C5–Cl6–Cl13 = 154.46(14)° and C6–Cl13–Cl6 = 135.93(15)°) as those to chloride ions. Two linear C–Cl–Cl angles would involve an unfavorable electrostatic interaction between two positive σ holes. An electrostatically optimum arrangement would be one linear angle and one nearly orthogonal. Our example appears to be in between, which possibly reflects the influence of crystal-packing effects. Indeed, *Desiraju* and coworkers classified these as Type I halogen bonds and found that they are largely due to dispersive interactions.[56,57]

Similar to the chloride ions in [**1**]$_2$[OH_3Cl_3]·CH_2Cl_2, all three chloride ions in the chloroform solvate have a trigonal pyramidal coordination geometry with acute angles between the halogen bond and hydrogen bonds, varying between 66° and 89° (*Table 8S*).

The salt [C_3(N^iPr_2)$_2$Br]Br·$C_2H_4Br_2$ crystallizes in the monoclinic space group $P2_1/n$. The asymmetric unit contains one cation, one bromide and one 1,2-dibromoethane solvate (*Figure 3*). The cation **2**$^+$ has a very similar structure to that of **1**$^+$ in the cations described above. The ring C–C distances are essentially the same: C1–C2 = 1.418(5) Å *versus* 1.429(3)–1.434(5) Å; and C2–C3 and C1–C3 = 1.368(5) Å *versus* 1.360(3)–1.379(5) Å. The C–Br distance of 1.852(4) Å is slightly shorter than in the dibromoethane solvate (1.885(7) and 1.946(6) Å). The bromide anion has a halogen bond with **2**$^+$ (Br1–Br2 = 3.2242(6) Å; Br1–Br2–C3 173.93(12)°) along with weak hydrogen bonds to dibromoethane (Br1–H5 A = 2.7524(4) Å) and an isopropyl CH group (Br1–H11 = 2.8695(4) Å) (*Figure 4*, *Table 11S*). Other hydrogen bonds to the bromide are much weaker (there are five Br–H distances to methyl protons in the range of 3.0–3.3 Å). The σ hole on a bromo substituent is significantly greater than for a chloro substituent, and, consequently, the halogen bonds are stronger and usually shorter, despite the larger size of Br *versus* Cl. The Br^-–Br halogen bond here is similar to what we have observed in a variety of octahalides (2.914–3.314 Å)[42–44] while *Kukushkin* reported a halogen bond distance of 3.3137(8) Å between Br^- and CH_2Br_2.[18] *Beer* and co-workers reported similar Br–Br halogen-bond distances in bromo-imidazolium bromide salts of 3.2968(4), 3.2652(13) and 3.1888(14) Å (R_D = 0.865, 0.857 and 0.837, resp.).[16] With an atomic

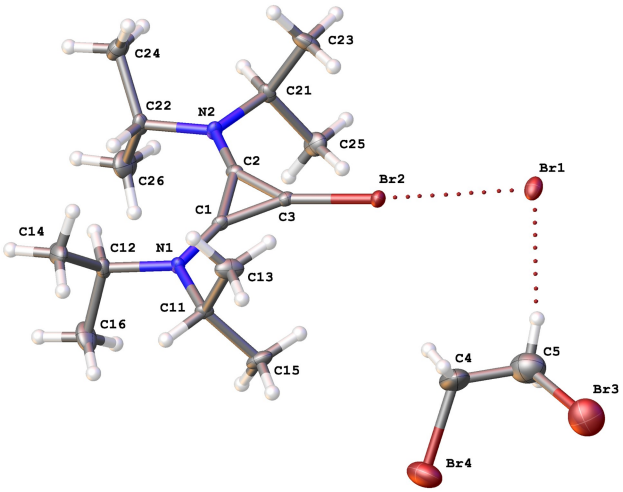


Figure 3. Thermal ellipsoid plot of the asymmetric unit of [**2**]Br·$C_2H_4Br_2$ with the atomic-labelling scheme.

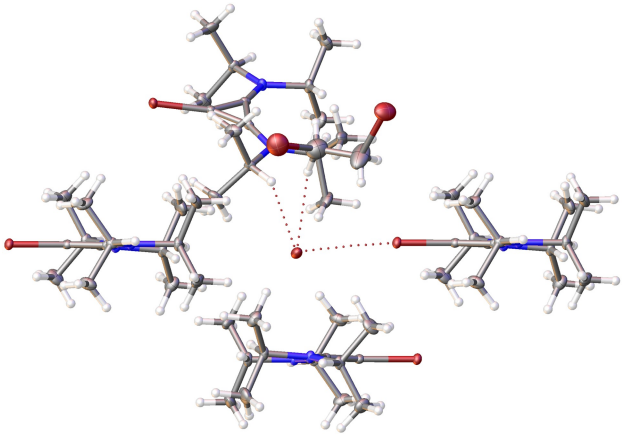


Figure 4. Coordination environment of the bromide ion in [**2**]Br.$C_2H_4Br_2$.

radius of 1.85 Å for Br and an effective ionic radius of 1.96 Å for Br^-,[47,48] R_D (0.846) in [**2**]Br is indeed significantly smaller than for the chloro-chloride halogen bonds (*Table 1*).

The bromide coordination geometry is again trigonal pyramidal for the three strongest halogen- and hydrogen-bonding interactions: Br2–Br1–H5 A = 80.062(11)°; Br2–Br1–H11 = 96.636(14)°; H5 A–Br1–H11 = 59.466(8)° (sum = 236.2°).

The octahalide salt $[\mathbf{1}]_2I_4Cl_4$ was found to crystallize in the monoclinic space group *I*2/*a* with one cation (*Figure 5*) and half of an octahalide in the asymmetric unit, with the other half generated by a C_2 axis (*Figure 6,a*). The structural parameters of the $\mathbf{1}^+$ cation are essentially identical to the other examples of $\mathbf{1}^+$ described here. The anion is an $[I_4Cl_4]^{2-}$ octahalide in

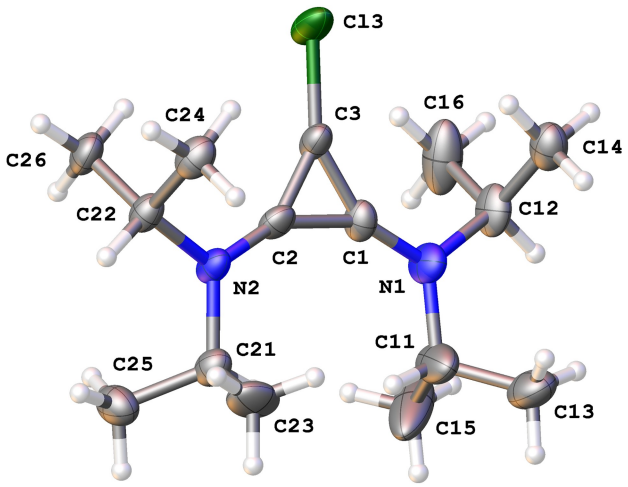


Figure 5. Atomic-labelling scheme for the cation in $[\mathbf{1}]_2I_4Cl_4$.

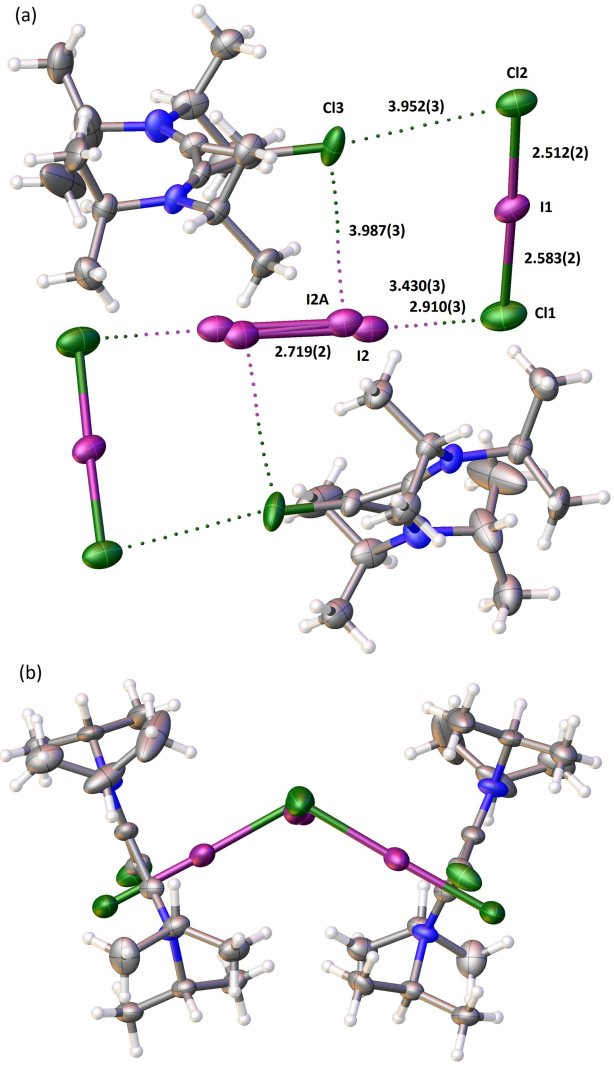


Figure 6. Thermal ellipsoid plots of $[\mathbf{1}]_2I_4Cl_4$: (a) the halogen-bonding and halogen-halogen distances of $I_4Cl_4^{2-}$. (b) View along the I_2Cl_2 axis (I1–Cl1–Cl1′–I1′ = 120.55(10)°).

which the central I_2 is disordered over two positions so as to effectively give a hybrid structure between an idealized symmetric octahalide with ordered and equivalent central I atoms, such as that which we reported earlier,[41] and an idealized pentahalide-trihalide structure, which would have symmetric trihalide and symmetric pentahalide fragments. The central I_2 distance of 2.719(2) Å is the same as in the symmetric anion 2.7245(10) Å, but the Cl–I halogen-bond distances of 3.430(3) Å and 2.910(3) Å are longer and shorter, respectively, than in the symmetric octahalide (3.125(2) Å). The terminal trihalide units have similar I–Cl distances (2.583(2) Å for I1–Cl1 and 2.512(2) Å for I1–Cl2) to the symmetric octahalide (2.592(2) Å and 2.504(2) Å). Another difference is that

whereas the symmetric octahalide is planar (this is the lowest energy conformation),[58] this example is twisted about the I_2Cl_2 axis (*Figure 6,b*). The barrier to this twist is typically very low.[58]

The distance between the chloro substituent of $\mathbf{1}^+$ and the terminal chloride of the octahalide is very long at 3.952(3) Å (Cl2–Cl3) and would not be considered as a halogen bond ($R_D = 1.110$). However, the σ hole on the chloro group points at the terminal chloride (C3–Cl3–Cl2 = 171.4(2)°) and the Cl3–Cl2–I1 angle of 74.90(6)° is also consistent with a σ hole interaction, just as the I1–Cl1–I2/I2 A angles are similarly perpendicular at 91.65(9)° and 89.32(8)°, respectively. Indeed, the terminal chloride Cl2 can be considered to have a very strong halogen bond with ICl and, consequently, a very weak halogen bond to $\mathbf{1}^+$. Nonetheless, further evidence against this being a halogen bond is that there is also a chloro-iodine interaction (Cl3–I2 A) with a similar distance of 3.987(3) Å (the sum of the Cl and I *van der Waals* radii is 3.73 Å). Although this is perpendicular to both the I–I axis (Cl3–I2 A–I2 = 85.80(7)°) and the C–Cl axis (C3–Cl3–I2 A = 88.6(2)°) which would not normally be favorable for a halogen bond.

Infrared Spectroscopy of the Hydronium Trichloride

The hydronium trichloride cluster was also studied by mid- and far-infrared spectroscopy (*Figure 7*, *Table 4*). To assist in the band assignments, a partially deuterated sample containing a mixture of D_3O^+ and HD_2O^+ cations was also prepared. An idealized $[OH_3Cl_3]^{2-}$ cluster would have C_{3v} symmetry and would display two bands in the ν(OH) region: a symmetric A_1 band $\nu(OH_{sym})$ and a degenerate E band $\nu(OH_{asym})$. These are ν_{10} and ν_9, respectively, in *Figure 8*. The cluster in $[\mathbf{1}]_2[H_3O]Cl_3\cdot CH_2Cl_2$ has crystallographic C_1 symmetry, but is close to C_s symmetry with one short hydrogen bond and two long hydrogen bonds. Therefore, we might expect to see splitting of the E band. The vibrational bands were also calculated for a gas phase $[OH_3Cl_3]^{2-}$ cluster, as well as all the H/D isotopomers, at the MP2/6-311++G(3d,2p) level (*Table 4*). Full details are given in the *Supporting Information*.

The $\nu(OH_{sym})$ band is calculated to be at 2690 cm^{-1}. A weak band at 2876 cm^{-1} does not change in intensity upon deuteration, so we instead assign the band at 2811 cm^{-1}, which is lost upon deuteration, to this transition.

The most intense band occurs for the degenerate $\nu(OH_{asym})$ E stretching mode ν_9 and is calculated to be at 2481 cm^{-1}, which we observe experimentally at 2681 cm^{-1} with a significant side band at 2656 cm^{-1} that may be due to splitting because of the lower symmetry in the solid state. A strong sharp band at 2482 cm^{-1} is assigned to a combination band (see below). Note that a significant band appears for a vibration of the cyclopropenium C_3 ring at 1911 cm^{-1}.

Stoyanov et al. reported quite different and very broad and overlapping IR bands for the chlorinated carborane salt $[H_3O][CHB_{11}Cl_{11}]$ at 3224 and 2911 cm^{-1} as well as a weak bending mode at 1602 cm^{-1}.[59] They also reported an inverse relationship between the stretching frequency and the bending frequency for a

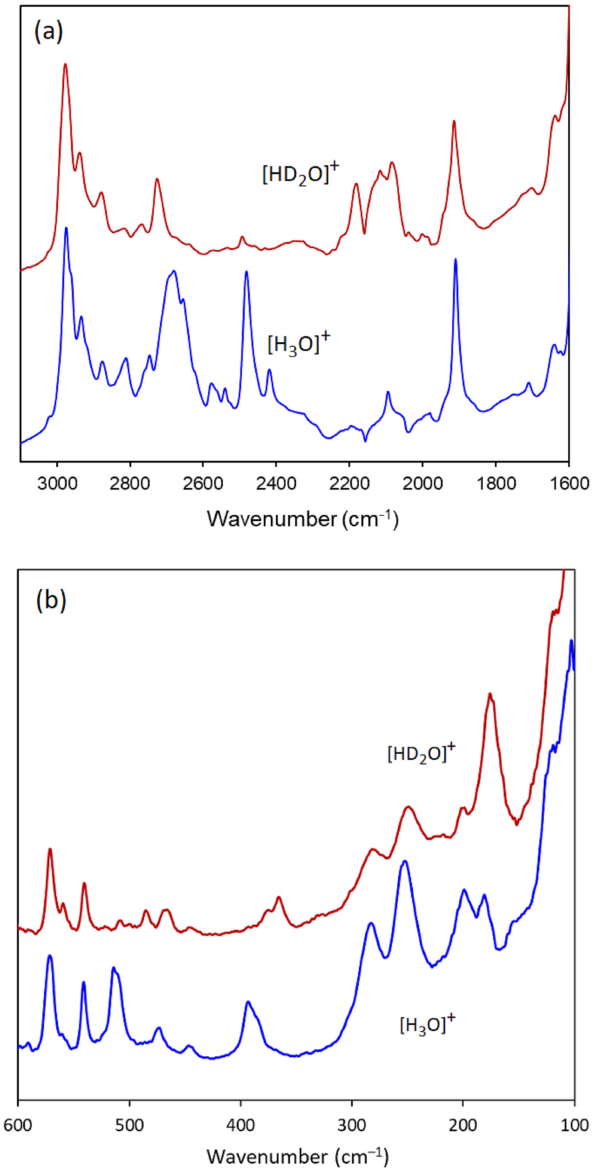


Figure 7. Mid (top) and far (bottom) infrared spectra of $[\mathbf{1}]_2[H_3O]Cl_3\cdot CH_2Cl_2$ and $[\mathbf{1}]_2[HD_2O]Cl_3\cdot CH_2Cl_2$.

Table 4. Experimental and calculated vibrational frequencies for $[OH_3Cl_3]^{2-}$ and $[OHD_2Cl_3]^{2-}$/$[OD_3Cl_3]^{2-}$.

$[OH_3Cl_3]^{2-}$ Experimental	Calc.[a]	Assignment	$[OHD_2Cl_3]^{2-}$/$[OD_3Cl_3]^{2-}$ Experimental	Calc.[a]	Assignment
2811	2690	ν_{10}	2725	2589	ν(O–H)
2681, 2656	2481	ν_9	2180	1890	ν(ODsym)
			2118	1848	ν(ODasym)
2482	2351	$\nu_6 + \nu_8$			
			2083	1842	ν_9 $[OD_3Cl_3]^{2-}$
514		$2\nu_4$	486		$2\nu_4$ $[OHD_2Cl_3]^{2-}$
			465		$2\nu_4$ $[OD_3Cl_3]^{2-}$
393		$\nu_3 + \nu_4$	375		$\nu_3 + \nu_4$ $[OHD_2Cl_3]^{2-}$
			365		$\nu_3 + \nu_4$ $[OD_3Cl_3]^{2-}$
283	269	ν_4	282	259	ν_4
252	269	ν_4	249	259	ν_4
200		Cation	200		Cation
180	230	ν_3	176	226	ν_3

[a] Calculated (and scaled) at the MP2/6-311 + + G(3d,2p) level.

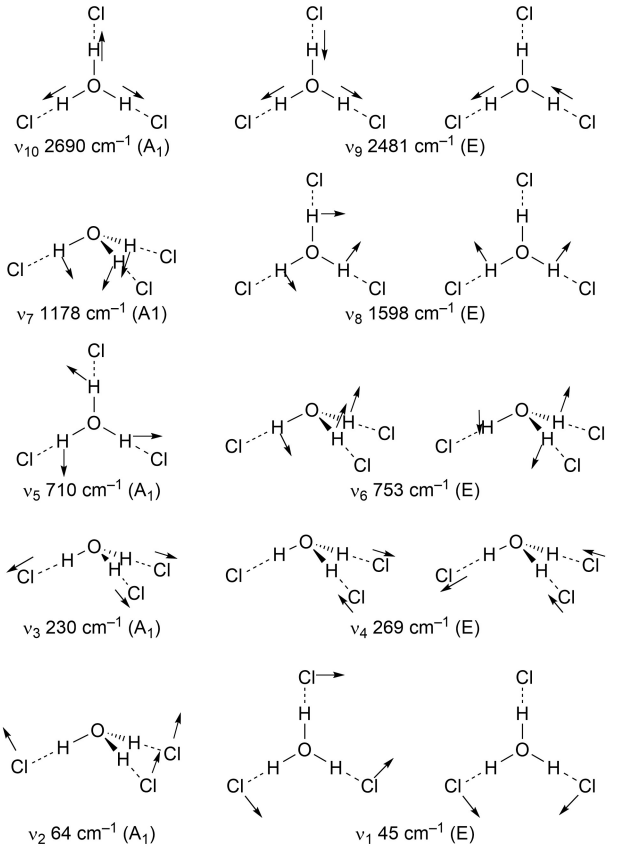


Figure 8. Calculated fundamental vibrational modes of $[OH_3Cl_3]^{2-}$.

series of hydronium salts. On the other hand, *Desbat* and *Huong* reported *Raman* bands at 2895, 2630 and 2525 cm^{-1} for $[H_3O]Cl$, which are at similar energies to the bands we observe due to also having strong hydrogen bonding to chloride ions.[60] Additionally, they report bending vibrational modes at 1650 and 1615 cm^{-1}. We do observe a weak band at 1640 cm^{-1}, however, this does not disappear upon deuteration and is also present in the infrared spectrum of [**1**]Cl·2$CHCl_3$ (*Supporting Information*), so it is unlikely to be this band. The calculated intensity for the degenerate H_3O^+ bending mode ν_8 at 1598 cm^{-1} is also extremely low and is probably why we do not see it. A significant band is calculated to occur at 1178 cm^{-1} due to the A_1-symmetric H_3O^+ bending mode ν_7. It is possible that the band at 2482 cm^{-1} is an overtone of ν_7 ($[ClHOH]^-$ shows a strong overtone of the H_2O bending mode).[61] However, we favor a combination band from the ν_8 $H_3O^+{}_{asym}$ bending mode at 1598 cm^{-1} and the ν_6 mode calculated to be at 753 cm^{-1} (sum = 2351 cm^{-1}). These bands are very similar in nature with both being a mix of degenerate bending and stretching modes, but with different relative amounts.

The partially-deuterated $[OHD_2Cl_3]^{2-}$ cluster would be expected to have a ν(OH) band intermediate between $\nu(OH_{sym})$ and $\nu(OH_{asym})$ of $[OH_3Cl_3]^{2-}$, and this appears in the expected place at 2725 cm^{-1}. Statistically, we would also expect to see some of either $[OH_2DCl_3]^{2-}$ or $[OD_3Cl_3]^{2-}$, however, there are no other bands in the ν(OH) region, thus ruling out the presence of $[OH_2DCl_3]^{2-}$. In the ν(OD) region, there are three bands, at 2180, 2118 and 2083 cm^{-1}. We assign the 2180 and 2118 cm^{-1} bands to $\nu(OD)_{sym}$ and $\nu(OD)_{asym}$, respectively, of $[OHD_2Cl_3]^{2-}$ and the 2083 cm^{-1} band to the E band, $\nu(OD)_{asym}$, of $[OD_3Cl_3]^{2-}$. The symmetric stretching band for this

cluster would be weaker and probably overlapping with the $[OHD_2Cl_3]^{2-}$ bands.

In the far-infrared, fundamental bands below 500 cm^{-1} are calculated to be very similar in energy for all isotopomers. Asymmetric and symmetric H_3O^+–Cl_3 liberational stretching modes ν_4 and ν_3, respectively, are calculated to occur at 269 and 230 cm^{-1}, respectively, compared to *ca.* 200 cm^{-1} for $[ClHOH]^-$.[45] We possibly see a splitting of the degenerate ν_4 into bands at 283 and 252 cm^{-1} for $[OH_3Cl_3]^{2-}$ and, similarly, 282 and 249 cm^{-1} for $[OHD_2Cl_3]^{2-}$. We assign ν_3 to the band at 180 cm^{-1} due to its change of intensity (possibly due to the mixture of OHD_2^+ and OD_3^+). Weaker bands at 514 and 393 cm^{-1} in the spectrum of $[OH_3Cl_3]^{2-}$ (which disappear upon deuteration) may be overtone and combination bands $2\nu_4$ and $\nu_3 + \nu_4$, respectively. These bands appear to split in the spectrum of $[OHD_2Cl_3]^{2-}$/$[OD_3Cl_3]^{2-}$ to bands at 486/465 and 375/365 cm^{-1}, respectively, due to the presence of the two isotopomers $[OH_2DCl_3]^{2-}$ and $[OD_3Cl_3]^{2-}$.

Conclusion

We have presented four structures containing halocyclopropenium cations, three of which have significant chloro-chloride or bromo-bromide CX^+–X^- halogen bonds and one which probably does not have a halogen bond to an $[I_4Cl_4]^{2-}$ octahalide. The degree to which the co-crystallites of [**1**]Cl impact on the Cl···Cl^- halogen bond tentatively appears to depend on two factors: whether crystal-packing constraints allow the formation of a halogen bond (in the hydronium case one of the two independent cations does not form a halogen bond, despite the near linear C–Cl···Cl^- angle), and some dependence on the strength of other intermolecular interactions, such as hydrogen bonds, to the acceptor Cl^- ion. Note that the terminal chloride in the $[I_4Cl_4]^{2-}$ cluster can be considered to have a strong halogen bond to an ICl fragment which weakens the halogen bond to the cation. The halide ions have significant hydrogen bonds with alkylhalides and, in one case, a hydronium cation. In the absence of significant geometrical constraints, the coordination geometries of the halides involve approximately orthogonal angles, frequently less than 90°.

The vibrational modes of a hydronium trichloride cluster cation were studied by both computational studies and infrared spectroscopy, aided by the spectra of a partially-deuterated sample, which gave very good agreement with the calculated spectra.

Supporting Information

Synthesis and characterization details; crystallographic data, bond lengths and angles; Computational details (geometry and calculated frequencies); IR spectra. Crystallographic data (CDCC 2201393–2201396) is also available free of charge from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; E-mail: deposit@ccdc.cam.ac.uk.

Acknowledgements

Open Access publishing facilitated by University of Canterbury, as part of the Wiley - University of Canterbury agreement via the Council of Australian University Librarians.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Author Contributions Statement

M. S. A. carried out conceptualization, investigation (synthesis and characterization), formal analysis, and writing – original draft. *O. J. C.* carried out supervision, project administration, resources, formal analysis, writing – review and editing, and visualization. *M. R. W.* carried out the computational studies and contributed to writing – review and editing.

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Received November 16, 2022
Accepted November 23, 2022

