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Weakly Bound Dications | *Very Important Paper* |

Halogenated *closo*-Dodecaborate Anions Stabilize Weakly Bound $[(Me_3NH)_3X]^{2+}$ (X = Cl, Br) Dications in the Solid State

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Dedicated to Professor Rüdiger Mews on the occasion of his 75th birthday

Abstract: Cocrystallization of $[Me_3NH]_2[B_{12}Y_{12}]$ (Y = Cl, Br, I) with 1 equiv. of $[Me_3NH]X$ (X = Cl, Br) from acetonitrile/diethyl ether solution produced large colorless single crystals of $[(Me_3NH)_3X][B_{12}Y_{12}]$. Four different compounds of this type were prepared and structurally characterized. The compounds consist of weakly coordinating perhalogenated *closo*-dodecaborate $[B_{12}Y_{12}]^{2-}$ dianions and unprecedented weakly bound discrete $[(Me_3NH)_3X]^{2+}$ dications. The $[(Me_3NH)_3X]^{2+}$ dications are built up from a central halide anion and three $[Me_3NH]^+$ cations bound by N–H···X hydrogen bonds. The cations have a pyramidal structure, as determined by X-ray diffraction, which is in contrast to quantum-chemical calculations, which predict a trigonal-planar structure. While the $[(Me_3NH)_3Cl]^{2+}$ and $[(Me_3NH)_3Br]^{2+}$ cations were easily prepared, attempts to synthesize the corresponding $[(Me_3NH)_3F]^{2+}$ and $[(Me_3NH)_3I]^{2+}$ cations failed. Three further crystal structures containing the angulated $[(Me_3NH)_2X]^+$ cation stabilized by $[B_{12}Cl_{12}]^{2-}$, $[B_{12}Br_{12}]^{2-}$, or $[Me_3NB_{12}Cl_{11}]^-$ are reported as well.

Introduction

Halogenated *closo*-dodecaborate anions $[B_{12}Y_{12}]^{2-}$ (Y = F, Cl, Br, I) have become important weakly coordinating anions with high chemical, thermal, and electrochemical stability.[1] Their fluoro, chloro, and iodo derivatives have been frequently used, because they can be prepared by simple procedures in large amounts[2] or are commercially available. They were shown to stabilize reactive cations,[3] to act as counteranions in catalysis,[4] and to be part of solid superacids,[5] host–guest complexes,[6] and low-melting salts.[7] They are interesting materials for electrochemical applications,[8] as anions in solid-state ion conductors,[9] and in biochemistry,[10] and they show unprecedented behavior in the gas phase.[11] The *closo*-dodecaborates have a charge of –2, which results in higher lattice energies of the respective salts compared to those of salts of singly charged weakly coordinating anions. The higher lattice energy of salts containing dianions allows very weakly bound dications to be stabilized in the solid state.[12] Some time ago we reported the synthesis and crystal structure of the weakly bound $[Li_2(SO_2)_8]^{2+}$ dication.[13] This dication is lattice-stabilized by the weakly coordinating $[B_{12}Cl_{12}]^{2-}$ dianion in the solid state. This means that the Coulomb explosion of $[Li_2(SO_2)_8]^{2+}$ to give two $[Li(SO_2)_4]^+$ cations, which is thermodynamically favorable in the gas phase, is suppressed in the solid state by the high lattice energy of the dication/dianion salt. In line with this, $[Cs_2(NCMe)_2]^{2+}$ dications stabilized by $[B_{12}Y_{12}]$ (Y = Cl, Br, I)[14] and $[K_2(OH_2)_n]^{2+}$ (*n* = 2,4) dications stabilized by $[B_{12}F_{12}]^{2-}$ were reported as well.[15] Thus, perhalogenated dodecaborate anions $[B_{12}Y_{12}]^{2-}$ (Y = F, Cl, Br, I) are able to lattice-stabilize weakly bound dications in the solid state that otherwise would dissociate into two singly charged cations.

In the course of our investigations of the $[B_{12}Cl_{12}]^{2-}$ dianion as a weakly coordinating anion, we attempted to crystallize $[Me_3NH]_2[B_{12}Cl_{12}]$, which proved to be difficult. However, suitable crystals for X-ray diffraction are easily obtained from acetonitrile/diethyl ether solution, when an excess of $[Me_3NH]Cl$ is present. The crystal structure determination showed that the structure contains the discrete hydrogen-bonded $[(Me_3NH)_3Cl]^{2+}$ dication (**1b**). Surprisingly, no data is available in the literature on this and related simple $[(R_3NH)_3X]^{2+}$ cations.

Herein we report the syntheses and crystal structures of several salts containing the previously unknown $[(Me_3NH)_3Cl]^{2+}$ (**1b**) and $[(Me_3NH)_3Br]^{2+}$ (**1c**) dications. Compounds containing the related $[(Me_3NH)_2X]^+$ cations [X = Cl (**2b**), Br (**2c**)] were obtained as well. All cations are stabilized by perhalogenated *closo*-dodecaborates $[B_{12}Y_{12}]^{2-}$ (Y = Cl, Br, I)[1] or the recently reported $[Me_3NB_{12}Cl_{11}]^-$ anion.[16]

Results and Discussion

Synthesis

Cocrystallization of $[Me_3NH]_2[B_{12}Y_{12}]$ with 1 equiv. of $[Me_3NH]X$ from acetonitrile/diethyl ether solution produced large colorless single crystals of the title compounds [Equation (1)] that were suitable for single-crystal X-ray diffraction analysis.

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$$[\mathrm{Me_3NH}]\mathrm{X} + [\mathrm{Me_3NH}]_2[\mathrm{B_{12}Y_{12}}] \xrightarrow{\mathrm{H_3CCN,\ Et_2O}} [(\mathrm{Me_3NH})_3\mathrm{X}][\mathrm{B_{12}Y_{12}}]$$
$$\mathbf{1}[\mathrm{B_{12}Y_{12}}]$$
$$\mathrm{X} = \mathrm{Cl}\ (\mathbf{1b}),\ \mathrm{Br}\ (\mathbf{1c});\ \mathrm{Y} = \mathrm{Cl, Br, I} \qquad (1)$$

Addition of a second equivalent of $[\mathrm{Me_3NH}]\mathrm{X}$ led to crystals containing the $[(\mathrm{Me_3NH})_2\mathrm{X}]^+$ cation (**2**) [Equation (2)].

$$2\ [\mathrm{Me_3NH}]\mathrm{X} + [\mathrm{Me_3NH}]_2[\mathrm{B_{12}Cl_{12}}] \xrightarrow{\mathrm{H_3CCN,\ Et_2O}} [(\mathrm{Me_3NH})_2\mathrm{X}]_2[\mathrm{B_{12}Cl_{12}}]$$
$$[\mathbf{2}]_2[\mathrm{B_{12}Cl_{12}}]$$
$$\mathrm{X} = \mathrm{Cl}\ (\mathbf{2b}),\ \mathrm{Br}\ (\mathbf{2c}) \qquad (2)$$

In an analogous manner cocrystallization of $[\mathrm{Me_3NH}][\mathrm{Me_3NB_{12}Cl_{11}}]$[16] with 1 equiv. of $[\mathrm{Me_3NH}]\mathrm{Cl}$ gave $[(\mathrm{Me_3NH})_2\mathrm{Cl}][\mathrm{Me_3NB_{12}Cl_{11}}]$ containing the same $[(\mathrm{Me_3NH})_2\mathrm{Cl}]^+$ cation (**2b**) [Equation (3)]. Addition of further $[\mathrm{Me_3NH}]\mathrm{Cl}$ did not lead to the formation of the $[(\mathrm{Me_3NH})_3\mathrm{Cl}]^{2+}$ dication (**1b**).

$$[\mathrm{Me_3NH}]\mathrm{Cl} + [\mathrm{Me_3NH}][\mathrm{Me_3NB_{12}Cl_{11}}] \xrightarrow{\mathrm{H_3CCN,\ Et_2O}} [(\mathrm{Me_3NH})_2\mathrm{Cl}][\mathrm{Me_3NB_{12}Cl_{11}}]$$
$$\mathbf{2b}[\mathrm{Me_3NB_{12}Cl_{11}}] \qquad (3)$$

While numerous attempts to crystallize simple trimethylammonium salts of $[\mathrm{B_{12}Y_{12}}]^{2-}$ did not yield single crystals of suitable quality, addition of 1 or 2 equiv. of trimethylammonium halide led to large crystals of very good quality in a short time. The obtained compounds contain the unprecedented $[(\mathrm{Me_3NH})_3\mathrm{X}]^{2+}$ (X = Cl, Br) dication (**1**) or the $[(\mathrm{Me_3NH})_2\mathrm{X}]^+$ cation (**2**). Note that only two crystal structures of trialkylammonium salts of the type $[\mathrm{R_3NH}]_2[\mathrm{B_{12}Y_{12}}]$ with halogenated dodecaborates as counteranions have been published so far, that is, they have little tendency to crystallize.[11a,17]

Crystal Structures

Molecular Structures of the $[(\mathrm{Me_3NH})_3\mathrm{X}]^{2+}$ Dications (1)

The salts $\mathbf{1b}[\mathrm{B_{12}Y_{12}}]\cdot\mathrm{H_3CCN}$ (Y = Cl, Br, I) and $\mathbf{1c}[\mathrm{B_{12}Cl_{12}}]\cdot\mathrm{H_3CCN}$ crystallize isostructurally in the orthorhombic space group *Pnma*. In the Supporting Information selected features of the crystal packing are visualized. Exemplarily, part of the crystal structure of $\mathbf{1b}[\mathrm{B_{12}Br_{12}}]\cdot\mathrm{H_3CCN}$ is shown in Figure 1. The structure consists of $[\mathrm{B_{12}Br_{12}}]^{2-}$ dianions and $[(\mathrm{Me_3NH})_3\mathrm{Cl}]^{2+}$ (**1b**) dications. In cation **1b** a central chloride ion forms three N–H···Cl contacts to three cationic $[\mathrm{Me_3NH}]^+$ units resulting in a discrete cation with an overall charge of +2. The dication **1b** has a pyramidal structure and forms one additional very weak C–H···Cl contact to an acetonitrile molecule of solvation (Figure 1). The $[(\mathrm{Me_3NH})_3\mathrm{X}]^{2+}$ cations presented herein are unprecedented, and no other $[(\mathrm{R_3NH})_3\mathrm{X}]^{2+}$ (R = alkyl) cations are known to the best of our knowledge. However, the pyramidal $(\mathrm{N{-}H\cdots})_3\mathrm{Cl}$ structural motif has been seen before in the chloride complex of protonated tris(pyrazolyl)hydroborate.[18] The crystal structure of trimethylammonium chloride was obtained in 1968,[19] and that of the $[(\mathrm{Me_3NH})_2\mathrm{Cl}]^+$ cation (**2b**) was reported by Mootz and co-workers in 1997.[20]

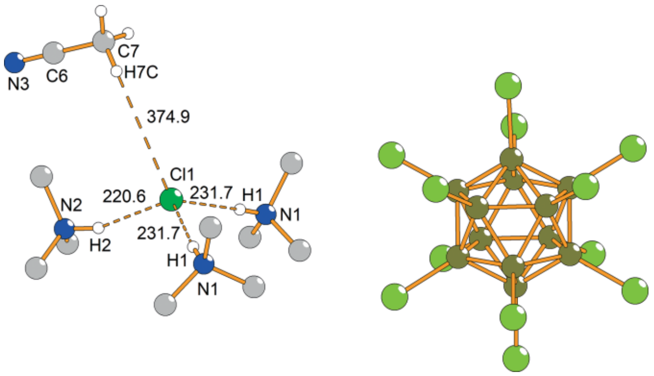


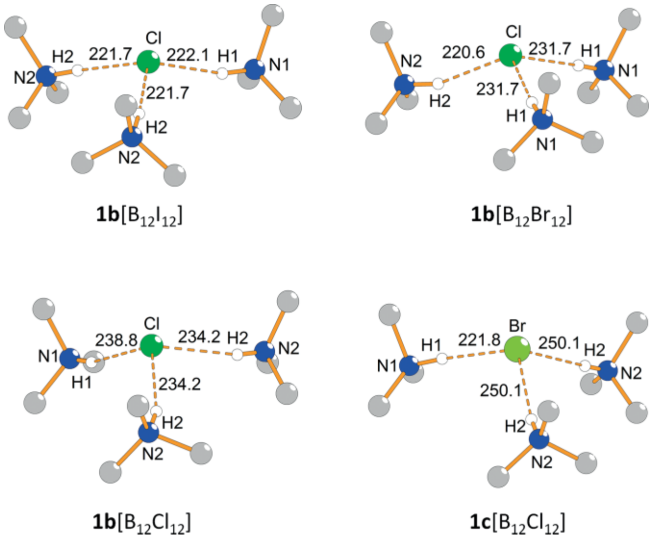
Figure 1. Part of the crystal structure of $[(\mathrm{Me_3NH})_3\mathrm{Cl}][\mathrm{B_{12}Br_{12}}]\cdot\mathrm{H_3CCN}$. The H···Cl distances are given in pm, and carbon-bonded hydrogen atoms are omitted for clarity.

Figure 2 shows the $[(\mathrm{Me_3NH})_3\mathrm{X}]^{2+}$ (**1**) cations in the crystal structures of $\mathbf{1b}[\mathrm{B_{12}Cl_{12}}]\cdot\mathrm{H_3CCN}$, $\mathbf{1b}[\mathrm{B_{12}Br_{12}}]\cdot\mathrm{H_3CCN}$, $\mathbf{1b}[\mathrm{B_{12}I_{12}}]\cdot\mathrm{H_3CCN}$, and $\mathbf{1c}[\mathrm{B_{12}Cl_{12}}]\cdot\mathrm{H_3CCN}$. Table 1 compiles selected averaged distances and angles for the $[(\mathrm{Me_3NH})_3\mathrm{X}]^{2+}$ cations. The cations have a pyramidal structure, and the sum of the N–X–N angles varies only slightly, between 330.1 and 338.3°, depending on the *closo*-dodecaborate counteranion. The Cl···H and N···Cl distances are within the expected range for strong N–H···Cl hydrogen bonds.[21] In comparison to the $[(\mathrm{Me_3NH})_2\mathrm{Cl}]^+$ cation (**2b**), the slightly longer distances suggest weaker hydrogen bonds in **1b** than in **2b**. The bromide-centered cation **1c** has a structure similar to that of **1b**. The N···Br distances are longer (av. 323.3 pm), in accord with the larger radius of the bromine atom. The sum of the N–Br–N angles is smaller than that in **1b**; thus, **1c** is more pyramidal.

The obtained structures are almost independent of the halogen substituents on the weakly coordinating $[\mathrm{B_{12}Y_{12}}]^{2-}$ anions. However, a closer look at the values in Table 1 reveals a clear trend. A longer H···Cl contact goes along with a shorter N···Cl distance and a smaller N–H···Cl angle. This might be caused by packing effects.

Table 1. Selected averaged distances and angles in the $[(\mathrm{Me_3NH})_3\mathrm{X}]^{2+}$ cation (**1**).

	Av. X···H distance [pm]	Av. N···X distance [pm]	Sum of the N–X–N angles [°]	Av. N–H–X angle [°]
$\mathbf{1b}[\mathrm{B_{12}Cl_{12}}]\cdot\mathrm{H_3CCN}$	235.7	311.8	330.1	161.6
$\mathbf{1b}[\mathrm{B_{12}Br_{12}}]\cdot\mathrm{H_3CCN}$	228.0	312.3	332.6	169.8
$\mathbf{1b}[\mathrm{B_{12}I_{12}}]\cdot\mathrm{H_3CCN}$	221.8	315.0	338.3	171.7
$\mathbf{1c}[\mathrm{B_{12}Cl_{12}}]\cdot\mathrm{H_3CCN}$	240.7	323.3	320.3	173.5



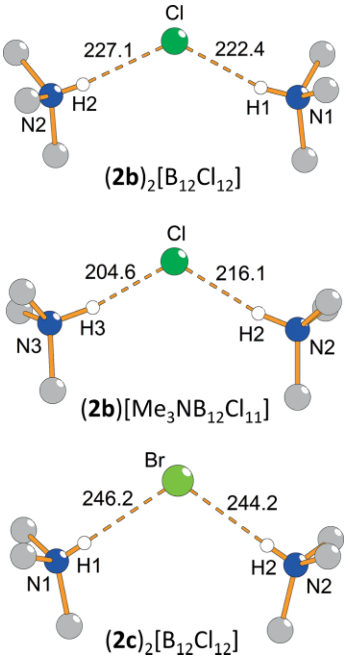
1b$[B_{12}I_{12}]$ **1b**$[B_{12}Br_{12}]$

1b$[B_{12}Cl_{12}]$ **1c**$[B_{12}Cl_{12}]$

Figure 2. Visualization of the $[(Me_3NH)_3X]^{2+}$ (**1**) cations in the crystal structures of **1b**$[B_{12}Cl_{12}]\cdot H_3CCN$, **1b**$[B_{12}Br_{12}]\cdot H_3CCN$, **1b**$[B_{12}I_{12}]\cdot H_3CCN$, and **1c**$[B_{12}Cl_{12}]\cdot H_3CCN$. The H···X distances are given in pm, and carbon-bonded hydrogen atoms are omitted for clarity.

Molecular Structures of the $[(Me_3NH)_2X]^+$ Cations (2)

Figure 3 shows the $[(Me_3NH)_2Cl]^+$ (**2b**) and $[(Me_3NH)_2Br]^+$ (**2c**) cations in the crystal structures of $[$**2b**$]_2[B_{12}Cl_{12}]$, **2b**$[Me_3NB_{12}Cl_{11}]\cdot H_3CCN$, and $[$**2c**$]_2[B_{12}Cl_{12}]\cdot 2H_3CCN$. All cations have an angulated structure. The N–X–N angle is larger for **2b** (124.8 or 130.8°) than for **2c** (110.2°). The N···Cl distances in **2b** vary between 302.7 and 307.5 pm, are significantly shorter than the sum of the van der Waals radii (330 pm),[22] are in the typical range for strong N–H···Cl hydrogen bonds,[21] and are slightly shorter than those of the $[(Me_3NH)_2Cl]^+$ cation in the crystal structure of **2b**$[HCl_2]$ (308.8 and 309.9 pm).[20] The H···Cl distances show a larger deviation and vary between 204.6 and 227.1 pm. The N···Br distances in **2c** are longer (319.6 and 320.4 pm) than the N···Cl distances in **2b**, in accord with a larger radius of the bromine atom.



(**2b**)$_2[B_{12}Cl_{12}]$

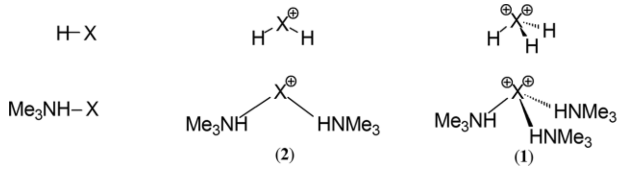
(**2b**)$[Me_3NB_{12}Cl_{11}]$

(**2c**)$_2[B_{12}Cl_{12}]$

Figure 3. Visualization of the $[(Me_3NH)_2X]^+$ (**2**) cations in the crystal structures of $[$**2b**$]_2[B_{12}Cl_{12}]$, **2b**$[Me_3NB_{12}Cl_{11}]\cdot H_3CCN$, and $[$**2c**$]_2[B_{12}Cl_{12}]\cdot 2H_3CCN$. The H···X distances are given in pm, and the carbon-bonded hydrogen atoms are omitted for clarity.

Comparison of 1 and 2 with the Parent Halonium Ions $[H_3X]^{2+}$ and $[H_2X]^+$

The $[(Me_3NH)_3X]^{2+}$ (**1**) and $[(Me_3NH)_2X]^+$ (**2**) cations are formally derived from the dicoordinate and tricoordinate halonium ions $[H_2X]^+$ and $[H_3X]^{2+}$ by formal replacement of the protons by trimethylammonium cations (Scheme 1).[23] While the parent halonium ions are experimentally unknown in condensed phase, several noncyclic dicoordinate chloronium compounds were synthesized and structurally characterized. Prominent recent examples are the dialkylchloronium ions $[R_2Cl]^+$ (R = Me, Et),[24] the bis(trimethylsilyl)chloronium ion $[(Me_3Si)_2Cl]^+$,[25] and the neutral $Me_2(B_{12}Cl_{12})$ molecule.[26] Much less is known about the respective tricoordinate dicationic chloronium ions $[R_3Cl]^{2+}$. Extensive theoretical investigations revealed a C_{3v}-symmetric structure for the parent $[H_3Cl]^{2+}$ dication.[27] The chloronium ions have short, covalent element–halogen bonds. In contrast, the nature of the hydrogen–halogen bonds in cations **1** and **2** is significantly different, and they should be rather described as typical N–H···X hydrogen bonds.[21,28]



Scheme 1.

To gain some insight, DFT calculations at the PBE0/def2-TZVPP level of theory were performed. While the optimized structures of $[(Me_3NH)_3Cl]^{2+}$ (**1b**), $[(Me_3NH)_3Br]^{2+}$ (**1c**), and $[(Me_3NH)_3I]^{2+}$ (**1d**) are planar, the structure of $[(Me_3NH)_3F]^{2+}$ (**1a**) was calculated to be pyramidal. Thus, the calculated structures of **1b** and **1c** are in contrast to the experimentally observed structures, which are pyramidal for $[(Me_3NH)_3X]^{2+}$ (X = Cl, Br). Similarly, the quantum-chemically optimized structures of the $[(Me_3NH)_2X]^+$ cations are linear, while the experimentally observed structures are bent. In an extreme case, as in the parent $[H_3X]^{2+}$ cations, a pyramidal structure is in accord with covalent H–X bonds and an electron lone pair residing on the halogen atom. At the other extreme, the trigonal-planar structure of the cation can be viewed as a purely ionic adduct of a negatively charged halide with three positively charged trimethylammonium cations. In this case the positively charged trimethylammonium cations arrange in a trigonal-planar manner around the central halide ion to minimize Coulomb repulsion. As discussed above, the N–H···X bond in the $[(Me_3NH)_3X]^{2+}$ cations is rather long and best described as a mainly ionic hydrogen bond. There is no simple explanation why the experimentally observed structures are pyramidal, while calculations predict planarity. Very likely the energy difference between planar and pyramidal structures in the $[(Me_3NH)_3X]^{2+}$ cations is small, and packing effects play an important role.

Do the $[(Me_3NH)_3F]^{2+}$ (1a) and $[(Me_3NH)_3I]^{2+}$ (1d) Cations Exist?

In analogy to Equation (1), experiments were carried out to cocrystallize $[Me_3NH]F$ or $[Me_3NH]I$ with $[Me_3NH]_2[B_{12}Cl_{12}]$. While different salts of the $[(Me_3NH)_3Cl]^{2+}$ and $[(Me_3NH)_3Br]^{2+}$ cations were easily prepared, all attempts to synthesize $[(Me_3NH)_3F]^{2+}$ and $[(Me_3NH)_3I]^{2+}$ cations were unsuccessful. From the reactions with $[Me_3NH]I$ two different sorts of crystals were obtained, which were identified as $[(Me_3NH)_3Cl][B_{12}Cl_{12}]$ and unconsumed $[Me_3NH]I$. The presence of chloride in the product can be traced back to a chloride impurity in the hydrogen iodide used for the synthesis of $[Me_3NH]I$ (see Figure S2). No evidence for the formation of the iodide-centered dication $[(Me_3NH)_3I]^{2+}$ (**1d**) could be obtained.

From the reaction of $[Me_3NH]F$ with $[Me_3NH]_2[B_{12}Cl_{12}]$, designed to give the $([Me_3NH]_3F)^{2+}$ dication (**1a**), no single crystals of the expected product were obtained. Instead, $[Me_3NH]F$ reacted in a manner similar to hydrogen fluoride with the glass of the reaction vessel to form hexafluorosilicate anions. These $[SiF_6]^{2-}$ anions cocrystallized in the double salt $[Me_3NH]_4[B_{12}Cl_{12}][SiF_6]\cdot 1.5H_3CCN$. Interestingly, the $[Me_3NH]^+$ cations exclusively form N–H···F contacts to the $[SiF_6]^{2-}$ anion, while no hydrogen bonding to the $[B_{12}Cl_{12}]^{2-}$ anion is observed. Thus, the $[SiF_6]^{2-}$ anion is more coordinating than the $[B_{12}Cl_{12}]^{2-}$ anion in this case. The coordination sphere around the $[SiF_6]^{2-}$ anion is visualized in Figure 4.

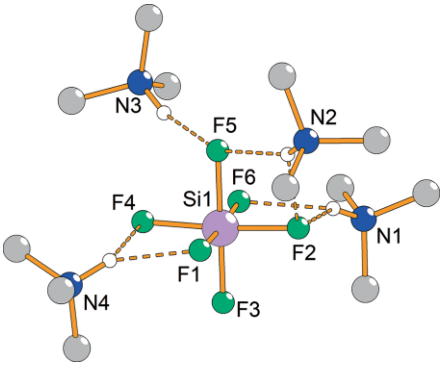


Figure 4. Part of the crystal structure of $[Me_3NH]_4[B_{12}Cl_{12}][SiF_6]\cdot 1.5H_3CCN$ showing the coordination sphere around the $[SiF_6]^{2-}$ anion. Carbon-bonded hydrogen atoms are omitted for clarity.

Clearly, the formation of the fluoro and iodo derivatives of the $[(Me_3NH)_3X]^{2+}$ dication (**1**) is less favorable. We suggest that the strength of the H···X hydrogen bond might be crucial. Calculated N–H stretching vibrations for the $[(Me_3NH)_3X]^{2+}$ cations show a significant difference between X = F (2612 cm^{-1}) and the other halogens (3023–3102 cm^{-1}). A lower calculated wavenumber for the N–H stretch corresponds to lower bond energy of the N–H bond and thus implies a stronger H···X interaction.[29] Therefore, cation **1a** can be viewed as $[H_3F]^{2+}\cdot(NMe_3)_3$ rather than as an $[(Me_3NH)_3F]^{2+}$ cation. Further support for the non-existence of the $[(Me_3NH)_3F]^{2+}$ cation comes from the calculated geometrical parameters of the anions. The H···F distances in $[(Me_3NH)_3F]^{2+}$ are very short (153 pm), in contrast to those in the chlorine (213 pm) and bromine derivatives (230 pm). This implies that there might be a steric problem. The short H···F bond leads to compression of the molecule and steric repulsion between the three NMe_3 groups.

Conversely, the non-existence of the $[(Me_3NH)_3I]^{2+}$ cation (**1d**) may be explained by the very weak H···I interaction. The calculated frequency of the N–H stretching vibration for the $[(Me_3NH)_3I]^{2+}$ cation (3102 cm^{-1}) is calculated to be the highest in this series and indicates a weak H···I hydrogen interaction. Along these lines the H···I bond in $[(Me_3NH)_3I]^{2+}$ is calculated to be the longest (253 pm). However, the weakness of the H···I hydrogen bond cannot be the only reason for our failure to prepare the $[(Me_3NH)_3I]^{2+}$ cation, because Schleid et al. were able to crystallize compounds containing $[(NH_4)_3I]^{2+}$ cations.[30] Another argument might be the N–X–N angle. According to the trend of averaged experimental N–X–N angles in $[(Me_3NH)_3X]^{2+}$ (**1b**: 110°; **1c**: 106°), the N–I–N angle would be smaller than 106°, which may lead to steric problems.

In conclusion, compounds containing **1a** or **1d** could not be prepared in this investigation under the selected physical and chemical conditions. The reasons remain unclear, and we cannot exclude that these cations may exist as well.

Importance of the Perhalogenated *closo*-Dodecaborates for the Formation of Cations 1 and 2

It is intriguing that cations of the type $[(Me_3NH)_3X]^{2+}$ (**1**) were unknown prior to this work, and only one example[20] of cations of the type $[(Me_3NH)_2X]^{+}$ (**2**) was reported. It appears that the weakly coordinating behavior of the perhalogenated *closo*-dodecaborates $[B_{12}Y_{12}]^{2-}$ facilitates the formation of these cations during the crystallization process. In contrast to other classes of weakly coordinating anions, the *closo*-dodecaborates carry a charge of –2, which causes a higher lattice energy of the respective salts. The higher lattice energy leads to reduced solubility and favors the formation of salts of the type $M^{2+}[B_{12}Y_{12}]^{2-}$, which has been demonstrated before on several occasions.[13–15] In addition, the spherical $[B_{12}Y_{12}]^{2-}$ anions tend to form distorted close-packed structures with large holes, which can be filled by suitable cations.

Conclusions

We could show that the chlorinated dianion $[B_{12}Cl_{12}]^{2-}$ is able to stabilize the dication **1b** as well as the monocation **2b** in the solid state, depending on the stoichiometry of the starting materials. In contrast, all reactions with the very closely related monoanion $[Me_3NB_{12}Cl_{11}]^-$ led to crystals of **2b**$[Me_3NB_{12}Cl_{11}]\cdot H_3CCN$ independently of the stoichiometry used. Thus, the particular properties of the $[B_{12}Y_{12}]^{2-}$ dianions seem to be crucial for the formation of the discrete weakly bound $[(Me_3NH)_3X]^{2+}$ (**1**) dications.

Experimental Section

General Remarks: All solvents and the following chemicals were used as purchased from the manufacturer: $[Me_3NH]Cl$ (Aldrich, 98 %), acetonitrile (VWR, HPLC grade), and diethyl ether (VWR). $[Me_3NH]_2[B_{12}Y_{12}]$ (Y = Cl, Br, I) were prepared from the corresponding sodium salts by metathesis reactions, as described in the literature.[2b,2c,31] The synthesis of $[Me_3NH]X$ (X = F, Br, I) is described in the Supporting Information. $[Me_3NH][Me_3NB_{12}Cl_{11}]$ was obtained according to a published procedure.[16b] IR spectra were measured with a Thermo Scientific Nicolet iS5 instrument equipped with an ID7 ATR unit and with a Nicolet Magna 760 spectrometer with a diamond ATR unit.

Preparation of Single Crystals: Single crystals suitable for X-ray diffraction of all compounds were obtained by the same general procedure. Slow diffusion of diethyl ether into an acetonitrile solution of $[Me_3NH]_2[B_{12}Y_{12}]$ (Y = Cl, Br, I) or $[Me_3NH][Me_3NB_{11}Cl_{11}]$ and an excess of $[Me_3NH]X$ (X = Cl, Br) yielded colorless crystals. Exemplarily, for the synthesis of $[(Me_3NH)_3Cl][B_{12}Y_{12}]$, $[Me_3NH]_2[B_{12}Y_{12}]$ (ca. 6 mg; Y = Cl, Br, I) and $[Me_3NH]X$ (0.8 mg; X = Cl) were dissolved in acetonitrile (5 mL). Slow diffusion of diethyl ether into the solution resulted in colorless crystals. $[(Me_3NH)_3Cl][B_{12}Cl_{12}]\cdot H_3CCN$: IR: $\tilde{\nu}$ = 3012 (vw), 2961 (w), 2861 (vw), 2608 (m), 2519 (sh), 2473 (m), 1478 (m), 1441 (w), 1412 (m), 1259 (m), 1242 (m), 1025 (s, $[B_{12}Cl_{12}]^{2-}$), 987 (vs), 819 (vw), 637 (w), 606 (m), 533 (s, $[B_{12}Cl_{12}]^{2-}$), 466 (w), 407 (vw). $[(Me_3NH)_3Cl][B_{12}Br_{12}]\cdot H_3CCN$: IR: $\tilde{\nu}$ = 3155 (vw), 3026 (vw), 2979 (w), 2730 (w), 1474 (m), 1465 (m), 1448 (w), 1414 (w), 1364 (w), 1064 (br.), 999 (sh, $[B_{12}Br_{12}]^{2-}$), 981 (vs, $[B_{12}Br_{12}]^{2-}$), 440 (s, $[B_{12}Br_{12}]^{2-}$). $[(Me_3NH)_3Cl][B_{12}I_{12}]\cdot H_3CCN$: IR: $\tilde{\nu}$ = 3143 (vw), 3109 (vw), 3020 (vw), 2977 (w), 2730 (m), 2515 (vw), 2464 (vw), 1594 (vw), 1462 (m), 1412 (m), 1363 (m), 1232 (w), 1204 (vw), 1053 (w), 981 (m), 938 (sh), 926 (vs, $[B_{12}I_{12}]^{2-}$), 457 (m). Full experimental details are available in the Supporting Information.

Crystal-Structure Determinations: Crystals suitable for X-ray diffraction analysis were obtained by slow diffusion of diethyl ether into an acetonitrile solution of $[Me_3NH]_2[B_{12}X_{12}]$ (X = Cl, Br, I) or $[Me_3NH][Me_3NB_{11}Cl_{11}]$ and an excess of $[Me_3NH]X$ (X = Cl, Br). The single-crystal X-ray diffraction studies were performed with an Oxford Diffraction Gemini E Ultra diffractometer equipped with a

Table 2. Crystal data and refinement results for **1**$[B_{12}Y_{12}]\cdot H_3CCN$ (X = Cl, Br; Y = Cl, Br, I).[a]

	1b$[B_{12}Cl_{12}]\cdot H_3CCN$	**1b**$[B_{12}Br_{12}]\cdot H_3CCN$	**1b**$[B_{12}I_{12}]\cdot H_3CCN$	**1c**$[B_{12}Cl_{12}]\cdot H_3CCN$
Empirical formula	$C_{11}H_{33}B_{12}Cl_{13}N_4$	$C_{11}H_{33}B_{12}Br_{12}ClN_4$	$C_{11}H_{33}B_{12}ClI_{12}N_4$	$C_{11}H_{33}B_{12}BrCl_{12}N_4$
M	811.98	1345.50	1909.38	856.44
Crystal system	orthorhombic	orthorhombic	orthorhombic	orthorhombic
Space group	*Pnma*	*Pnma*	*Pnma*	*Pnma*
a [pm]	2094.51(16)	2150.93(3)	2257.26(5)	2101.95(6)
b [pm]	1326.69(12)	1348.61(2)	1393.16(3)	1327.06(6)
c [pm]	1297.37(11)	1322.90(2)	1383.10(3)	1290.86(4)
α [°]	90	90	90	90
β [°]	90	90	90	90
γ [°]	90	90	90	90
V [nm^3]	3.6051(5)	3.83742(10)	4.34947(16)	3.6007(2)
Z	4	4	4	4
μ(Mo-K_α) [mm^{-1}]	1.012	12.611	8.621	2.049
No. of data collected	8076	64972	173194	18842
No. of unique data	2931	8702	14610	3653
R_{int}	0.0542	0.0470	0.0289	0.0360
R_1, wR_2 [$I > 2\sigma(I)$][a]	0.0613, 0.1393	0.0242, 0.0384	0.0225, 0.0476	0.0493, 0.1469
R_1, wR_2 (all data)	0.0895, 0.1484	0.0442, 0.0419	0.0264, 0.0489	0.0547, 0.1498

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[wF_o^4]\}^{1/2}$.

Table 3. Crystal data and refinement results for **2b**$[Me_3NB_{12}Cl_{11}]\cdot H_3CCN$, $[$**2b**$]_2[B_{12}Cl_{12}]$, $[$**2c**$]_2[B_{12}Cl_{12}]\cdot 2H_3CCN$, and $[Me_3NH]_4[B_{12}Cl_{12}][SiF_6]\cdot 1.5H_3CCN$.[a]

	2b$[Me_3NB_{12}Cl_{11}]\cdot H_3CCN$	$[$**2b**$]_2[B_{12}Cl_{12}]$	$[$**2c**$]_2[B_{12}Cl_{12}]\cdot 2H_3CCN$	$[Me_3NH]_4[B_{12}Cl_{12}][SiF_6]\cdot 1.5H_3CCN$
Empirical formula	$C_{11}H_{32}B_{12}Cl_{12}N_4$	$C_{12}H_{40}B_{12}Cl_{14}N_4$	$C_{16}H_{46}B_{12}Br_2Cl_{12}N_6$	$C_{15}H_{44.5}B_{12}Cl_{12}F_6N_{5.5}Si$
M	775.52	866.50	1037.71	999.27
Crystal system	monoclinic	triclinic	monoclinic	monoclinic
Space group	$P2_1/c$	$P\bar{1}$	$P2_1/c$	$P2_1/n$
a [pm]	1376.07(4)	1023.08(7)	1218.97(2)	1036.01(3)
b [pm]	1294.90(4)	1037.25(8)	1020.47(2)	3067.83(7)
c [pm]	2056.61(5)	1160.55(9)	1807.93(4)	1408.96(3)
α [°]	90	70.165(7)	90	90
β [°]	107.697(3)	65.428(8)	94.604(2)	90.204(3)
γ [°]	90	63.344(7)	90	90
V [nm^3]	3.49121(17)	0.98316(15)	2.24167(8)	4.47807(19)
Z	4	1	2	4
μ(Mo-K_α) [mm^{-1}]	0.967	0.998	2.547	1.482
No. of data collected	17681	6790	20075	16657
No. of unique data	8099	3653	4401	7874
R_{int}	0.0217	0.0266	0.0231	0.0246
R_1, wR_2 [$I > 2\sigma(I)$][a]	0.0335, 0.0772	0.0582, 0.1621	0.0410, 0.1098	0.0384, 0.0838
R_1, wR_2 (all data)	0.0480, 0.0846	0.0665, 0.1664	0.0449, 0.1121	0.0509, 0.0509

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[wF_o^4]\}^{1/2}$.

2 k × 2 k EOS CCD area detector and a four-circle kappa goniometer by using Mo-K_α (0.71073 Å) radiation or with a Bruker Smart Apex-II CCD system at 150 K. The crystals were mounted on a cryo loop by using fluorinated oil and frozen in the cold nitrogen stream of the goniometer. The structures were solved by direct methods (SHELXS)[32] with the program package OLEX2.[33] Subsequent least-squares refinement on F^2 (SHELXL)[34] located the positions of the remaining atoms in the electron-density maps. All non-hydrogen atoms were refined with anisotropic replacement factors. Carbon-bonded hydrogen atoms were placed in calculated positions by using a riding model. Nitrogen-bonded hydrogen atoms were identified from the electron-density map. The data were corrected for absorption. Crystallographic data is compiled in Tables 2 and 3, and further details are available in the Supporting Information. CCDC 1432381 (for **1b**$[B_{12}Cl_{12}]\cdot H_3CCN$), 1432382 (for **1b**$[B_{12}Br_{12}]\cdot H_3CCN$), 1432383 (for **1b**$[B_{12}I_{12}]\cdot H_3CCN$), 1432385 (for **1c**$[B_{12}Cl_{12}]\cdot H_3CCN$), 1432379 (for **2b**$[Me_3NB_{12}Cl_{11}]\cdot H_3CCN$), 1432380 (for [**2b**]$_2[B_{12}Cl_{12}]$), 1432384 (for [**2c**]$_2[B_{12}Cl_{12}]\cdot 2H_3CCN$), 1544964 (for $[Me_3NH]_4[B_{12}Cl_{12}][SiF_6]\cdot 1.5H_3CCN$) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

Quantum-Chemical Calculations: The structures were optimized at the PBE0/def2-TZVPP level of theory as implemented in the program package TURBOMOLE V6.3.[35] Frequency calculations were performed analytically by using the AOFORCE module. All calculated species are true minima on the energy hypersurface, as shown by the absence of imaginary frequencies. Further details are included in the Supporting Information.

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Keywords: Cations · Borates · Halides · Hydrogen bonds · Weakly coordinating anions

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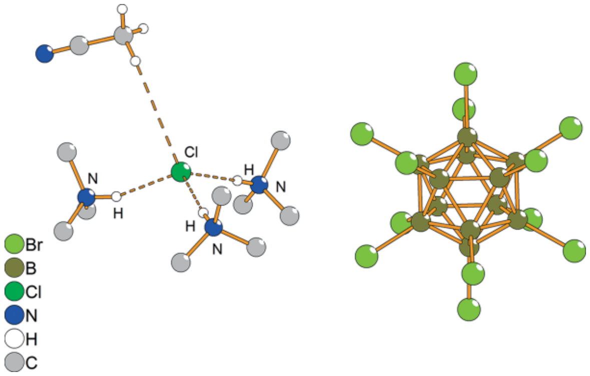
Weakly Bound Dications

Halogenated *closo*-Dodecaborate Anions Stabilize Weakly Bound $[(Me_3NH)_3X]^{2+}$ (X = Cl, Br) Dications in the Solid State



Unprecedented $[(Me_3NH)_3X]^{2+}$ dications are lattice-stabilized in the solid state by perhalogenated *closo*-dodecaborates. Syntheses of the materials and their crystal structures are discussed and compared with the results of quantum-chemical calculations.

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