
**From Polyinterhalides to Polypseudohalides:
Synthesis, Characterization and Applications
of Compounds Based on BrCl and BrCN**

Inaugural-Dissertation
to obtain the academic degree
Doctor rerum naturalium (Dr. rer. nat.)

submitted to the
Department of Biology, Chemistry, Pharmacy
of Freie Universität Berlin

by

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2020

The work for the present dissertation has been conducted between September 2016 and July 2020 under the guidance of Prof. Dr. Sebastian Hasenstab-Riedel at the Institute of Chemistry and Biochemistry (Department of Biology, Chemistry, Pharmacy) of Freie Universität Berlin.

Declaration of authorship:

I declare that I have completed the submitted dissertation independently and without the use of sources and aids other than those indicated. I have marked as such all statements that are taken literally or in content from other writings. This dissertation has not been submitted in the same or similar form in any previous doctoral procedure.

Berlin, 01. July 2020

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Day of Disputation: 02. October 2020

Acknowledgements

First, I want to express my gratitude to my doctoral advisor Prof. Dr. Sebastian Hasenstab-Riedel for the possibility to work in his working group in Berlin, for allowing me to work on this interesting topic and for the trust he placed in me. I will always remember the business trip to Regensburg, sunny Freiburg and the even sunnier San Francisco.

I also want to thank Prof. Dr. Christian Müller for accepting the position as second referee. I would like to thank the entire AC, the workshops, secretariats and all other members of the FU for their cooperation and help in numerous situations.

Thanks to Simon and Helmut for the scientific support in planning syntheses and writing my papers. Many thanks to Günther, Karsten, Marlon and Vossi for proof-reading this dissertation.

I would like to thank my students Hannes and Thomas for their hard work, which also applies to the many trainees, who spent their time in U406. Of course, a big thanks also goes to the entire former and current working group for a really good time in the past four years.

I would particularly like to emphasize Karsten, Marlon, Vossi, Gene, Tyler and Jan, who have not only become good colleagues, but rather very good friends. Many thanks to the Battery Boys, Max and Vossi, who helped making the "Labor der Liebe" the most successful, popular and atmospheric of the entire AG.

I also want to thank my friends from Göttingen, with whom I had wonderful studies with many highlights, such as the evenings with Ernest, the victory in the football cup, and marvelous Father's Day hikes.

By far, my deepest thanks go to all my friends (whether in Bad Harzburg, Göttingen or Berlin), my entire family and Caro. No matter what ups and downs I had in life, you always had my back, made me laugh, cheered me up, always believed in me and accepted me as I am. I truly love you!

To all of you:

Many, many thanks!

Danksagung

An erster Stelle möchte ich mich bei meinem Doktorvater Prof. Dr. Sebastian Hasenstab-Riedel bedanken, der es mir ermöglichte meine Promotion in seinem Arbeitskreis in Berlin durchzuführen. Bei Ihm bedanke ich mich für das interessante Thema und das Vertrauen in meine Fähigkeiten. Zudem werde ich die in meiner Promotion ermöglichten Dienstreisen nach Regensburg, in das sonnige Freiburg und vor allem in das noch sonnigere San Francisco stets in Erinnerung behalten.

Bei Prof. Dr. Christian Müller bedanke ich mich für die freundliche und bereitwillige Übernahme des Korreferats.

Der gesamten AC, den Werkstätten, Glasbläsern, Sekretariaten sowie allen übrigen Festangestellten der FU danke ich für die Kooperation und Hilfe in zahlreichen Situationen. Danke an Simon und Helmut für die wissenschaftliche Unterstützung bei der Planung von Synthesen und dem Schreiben der Paper. Vielen Dank an Günther, Karsten, Marlon und Vossi für die Hilfe beim Schreiben dieser Dissertation und für das Korrekturlesen.

Meinen Studenten Hannes und Thomas danke ich für ihre gute Arbeit, was auch für die vielen Auszubildenden, die ihre Zeit in U406 verbrachten, gilt. Natürlich gilt auch ein großer Dank der gesamten ehemaligen und derzeitigen Arbeitsgruppe für eine wirklich sehr schöne Zeit in den letzten vier Jahren.

Dabei möchte ich besonders Karsten, Marlon, Vossi, Gene, Tyler und Jan hervorheben, die nicht nur gute Kollegen, sondern vielmehr sehr gute Freunde geworden sind. Vielen Dank an die Battery Boys, Max und Vossi, die dazu beigetragen haben das Labor der Liebe zum erfolgreichsten, beliebtesten und stimmungsvollsten der gesamten AG zu machen.

Ich bedanke mich auch bei meinen Freunden aus Göttingen, mit denen ich eine wunderbare Studienzeit mit vielen Highlights, wie den Abenden bei Ernest, dem Sieg beim Fußballturnier sowie grandiosen Vatertagswanderungen, zu verdanken habe.

Mein mit Abstand größter Dank gilt aber allen meinen Freunden (egal ob in Bad Harzburg, Göttingen oder Berlin), meiner gesamten Familie und Caro. Egal welche Höhen und Tiefen ich im Leben hatte, ihr wart immer für mich da, habt mich zum Lachen gebracht, wieder aufgebaut, stets an mich geglaubt und mich so akzeptiert wie ich bin. Ich liebe euch!

An euch alle:

Vielen, vielen Dank!

List of Abbreviations

3c-4e	three-center four-electron
AO	atomic orbital
ATR-IR	attenuated total reflection infrared
aug-cc-PVTZ	augmented correlation-consistent polarized valence-only triple zeta
B3LYP	Becke, three-parameter, Lee-Yang-Parr
BJ	Becke-Johnson damping
BMP	1-butyl-1-methylpyrrolidinium
BMBF	Bundesministerium für Bildung und Forschung
Bu	<i>n</i> -butyl
C ₅ H ₁₀ N ₂ Br	<i>N,N'</i> -dimethyl-2-bromidoimidazolium
Cat	cation
CCDC	Cambridge Crystallographic Data Center
CCSD(T)	coupled cluster with single, double and perturbative triple excitations
CCl(NMe ₂) ₂	tetramethylchloroamidinium
COSMO	conductor-like screening model
D3	dispersion correction (Grimme)
DCM	dichloromethane
def2-TZVPP	valence triple zeta with two sets of polarization functions
DFT	density functional theory
ESI	electrospray ionization
ESP	electrostatic potential
Et	ethyl
EtOAc	ethyl acetate
HMIM	1-hexyl-3-methylimidazolium
HMET	1,6-bis(trimethylammonium)hexane
HOMO	highest occupied molecular orbital
HR-MS	high-resolution mass spectrometry
Ib15c5	diiodobenzo-15-crown-5

IL	ionic liquid
IR	infrared
IUPAC	International Union of Pure and Applied Chemistry
LUMO	lowest unoccupied molecular orbital
Me	methyl
MeCN	acetonitrile
MeOH	methanol
MO	molecular orbital
MP2	second-order Møller-Plesset perturbation
NMR	nuclear magnetic resonance
NTf ₂	bis(trifluoromethylsulfonyl)imide (triflimide)
OTf	trifluoromethanesulfonate, (triflate)
[P ^{666,14}] ⁺	trihexyltetradecylphosphonium
Ph	phenyl
PNP	bis(triphenylphosphine)iminium
Pr	<i>n</i> -propyl
RI	resolution of identity
RT-IL	room temperature ionic liquid
SCS	Spin-Component Scaling
SCS-MP2	Spin-Component Scaled second-order Møller-Plesset perturbation
SI	Supporting Information
τ	Addison's geometric parameter
VSEPR	valence shell electron pair repulsion
XRD	X-ray diffraction
X, Y, Z	halogen atom

Abstract

Polyhalogen chemistry receives great attention due to its structural diversity and increasing possible applications. This diversity can be expanded by using interhalogens, such as BrCl, exploiting its more pronounced σ -hole compared to the halogens Cl₂ and Br₂. However, because of its equilibrium with Cl₂ and Br₂, the stoichiometric usage of neat BrCl as a reagent is hampered. Consequently, an improved *in situ* synthesis route for BrCl based interhalogen compounds is introduced. The presented addition of a halogen bond acceptor (e.g. Cl⁻) results in an almost entire shift of the equilibrium to the BrCl side (>99.99 %). This enables the stabilization and crystallographic characterization of a complete set of non-classical polyinterhalogen monoanions [Cl(BrCl)_n]⁻ ($n = 2 - 6$), which consist of a central chloride that is coordinated by two to six BrCl molecules, respectively. The reported octahedral structural motif of the [Cl(BrCl)₆]⁻ monoanion in [PNP][Cl(BrCl)₆] is very rare in polyhalogen chemistry and represents the first tridecahalogen anion. Additionally, easy-to-handle room temperature ionic liquids based on BrCl have been investigated in interhalogenation reactions of alkenes, alkynes and Michael systems.

As a further development, it was possible to expand the concept of halogen bonding to the pseudohalogen cyanogen bromide (BrCN). Accordingly, the non-symmetric pseudohalogen BrCN can be compared to interhalogens such as IBr and BrCl. Herein, a new class of polypseudohalogen compounds based on BrCN, including the almost linear [Br(BrCN)]⁻ as well as the distorted trigonal-pyramidal [Br(BrCN)₃]⁻, is presented. Both structures were characterized by XRD, Raman spectroscopy and quantum-chemical calculations. Moreover, the dynamic behavior of these compounds in solution and as room temperature ionic liquid was studied by ¹³C and ¹⁵N NMR spectroscopy. The significantly reduced vapor pressure of these reactive ionic liquids compared to neat BrCN, combined with the ability to dissolve elemental gold are promising applications for ongoing research.

Kurzzusammenfassung

Die Polyhalogenchemie erfreut sich aufgrund ihrer strukturellen Vielfalt und der steigenden Anwendungsmöglichkeiten großer Aufmerksamkeit. Diese Vielfalt kann durch Interhalogene wie BrCl erweitert werden, indem sein deutlicher ausgeprägtes σ -Loch im Vergleich zu den Halogenen Cl₂ und Br₂ ausgenutzt wird. Aufgrund des Gleichgewichts mit Cl₂ und Br₂ ist stöchiometrisches Arbeiten mit gasförmigen BrCl als Reagenz jedoch nahezu unmöglich. Daher wurde eine verbesserte *in situ* Synthese für Interhalogenverbindungen auf BrCl-Basis präsentiert. Die hier vorgestellte Zugabe eines Halogenbindungsakzeptors (z. B. Cl⁻) führt zu einer fast vollständigen Verschiebung des Gleichgewichts auf die BrCl-Seite (>99,99 %). Dies ermöglicht die Stabilisierung und kristallographische Charakterisierung einer vollständigen Reihe nicht-klassischer Polyinterhalogenmonoanionen [Cl(BrCl)_n]⁻ ($n = 2 - 6$), welche aus einem zentralen Chlorid aufgebaut sind, das von zwei bis sechs BrCl-Molekülen koordiniert wird. Die beschriebene oktaedrische Struktur des [Cl(BrCl)₆]⁻ Monoanions in [PNP][Cl(BrCl)₆] ist in der Polyhalogenchemie äußerst selten und stellt das erste Tridecahalogenanion überhaupt dar. Darüber hinaus wurden einfach zu handhabende Raumtemperatur-ionische-Flüssigkeiten auf Basis von BrCl in Interhalogenierungsreaktionen von Alkenen, Alkinen und Michael-Systemen untersucht.

Weiterhin konnte das Konzept der Halogenbindung auf das Pseudohalogen Bromcyan (BrCN) erweitert werden. Dementsprechend kann das asymmetrische Pseudohalogen BrCN mit Interhalogenen wie IBr und BrCl verglichen werden. Im Rahmen dieser Arbeit wird eine neue Klasse von Polypseudohalogenverbindungen basierend auf BrCN vorgestellt. Darunter zählen das nahezu lineare [Br(BrCN)]⁻ sowie das verzerrt trigonal-pyramidale [Br(BrCN)₃]⁻. Beide Strukturen wurden mittels XRD, Ramanspektroskopie und quantenchemischer Rechnungen charakterisiert. Zusätzlich wurde das dynamische Verhalten der neuen Verbindungen in Lösung und als Raumtemperatur-ionische-Flüssigkeit durch ¹³C- und ¹⁵N-NMR-Spektroskopie untersucht. Der im Vergleich zu reinem BrCN deutlich verringerte Dampfdruck dieser reaktiv-ionischen-Flüssigkeit sowie deren Fähigkeit elementares Gold aufzulösen, sind vielversprechende Anwendungsmöglichkeiten für zukünftige Forschungen.

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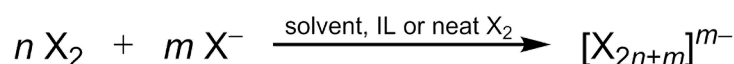
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1. Introduction

In the periodic table, the only group that contains elements in three states of matter at ambient conditions is the group of the halogens. These halogens, comprising solid iodine, liquid bromine as well as gaseous chlorine and fluorine, are important raw materials for industrial applications. With a yearly production of 75 million tons, chlorine is the most significant halogen and is mainly used for the fabrication of polymers, molecular drugs and agrochemicals.^[1] Industrial use of the other halogens range, for example, from the production of flame retardants^[2] (bromine) and contrast agents in medical imaging^[3] (iodine) to membranes in fuel cells (fluorine).^[4] In addition to their wide use for industrial purposes, halogens are of great scientific interest as well. The highly reactive elements not only react with other substances but also with each other and are able to form neutral, cationic, or anionic compounds. In 1819, Pelletier and Caventou observed attractive interactions between halogens and halide ions and discovered the first formation of a polyhalogen monoanion (often referred to as “polyhalide”), the triiodine monoanion $[I_3]^-$, which serves as the starting point of polyhalogen research that has been going on for over two centuries.^[5]

1.1. Bonding Situation in Polyhalogen Anions

In first systematic investigations of polyhalogen monoanions in 1923, Chattaway and Hoyle added halogens to a solution of the corresponding tetraalkylammonium halide in acetic acid or alcohol. They observed the formation of new species, which were analyzed by their physical properties and by gravimetry. Furthermore, they found out that bromide and chloride salts were able to absorb large amounts of the corresponding halogen.^[6] Nowadays, the synthesis of polyhalogen compounds has changed only slightly. In general, polyhalogen anions are synthesized by adding a halogen to a halide salt, see Equation 1.^[7]



Equation 1. General synthesis route for polyhalogen anions.

However, these reactions can be carried out in solvents^[8], ionic liquids^[9,10] or in the neat halogens^[11,12]. This variation of the reaction conditions has an influence on the polyhalogen anion and is discussed in detail in the following section.

Most of the larger polyhalogen monoanions are built of the three basic building blocks X^- , $[X_3]^-$ and X_2 and can be defined as donor-acceptor complexes. Usually, the Lewis base X^- or $[X_3]^-$,

located in the center of the polyhalogen molecule, donates electron density from the highest occupied molecular orbital (HOMO) into the lowest unoccupied molecular orbital (LUMO, σ^*) of the coordinating halogen molecules X_2 , the Lewis acids. This charge transfer results in a bond weakening and therefore an elongation of the X–X bond, which can be observed both quantum-chemically and experimentally. The distance between the Lewis base and Lewis acid has to be within the sum of the van der Waals radii, in order to consider the coordinating molecule as a part of the polyhalogen anion.^[7,13] Shaik and co-workers systematically studied the bonding situation in polyhalogen monoanions $[X_{2n+1}]^-$ ($X = \text{Cl}, \text{Br}; n = 1 - 5$) using the block-localized wave function (BLW) that offers a valence bond analysis.^[13] Their investigations validate the dominant role of the charge transfer between the lone pair of X^- and the antibonding orbital ($n \rightarrow \sigma^*$) of the coordinating X_2 molecule. As a result, the studied bonding situation in polyhalogen monoanions is essentially of dative-covalent character. Furthermore, the charge transfer interactions in $[X_{2n+1}]^-$ are decreasing with increasing n , which is in accordance with the weakening of the Lewis basicity. In summary, Shaik and co-workers argued, that the bonding between X^- and n X_2 molecules in larger anions is based on the bonding situation of trihalogen monoanions $[X_3]^-$.^[13]

However, $[X_3]^-$ and its bonding situation can be considered as a special case and is subject of current research.^[14] For an asymmetric trihalogen anion ($[X \cdots X-X]^-$), the bonding situation can be described as a donor-acceptor complex, as stated above. In the case of a symmetric trihalogen monoanion in $D_{\infty h}$ symmetry, a three-center four-electron bond (3c-4e) can be formulated. The 3c-4e bond results in an overall bond order of 0.5, which explains the elongated X–X bond lengths, see Figure 1.^[7]

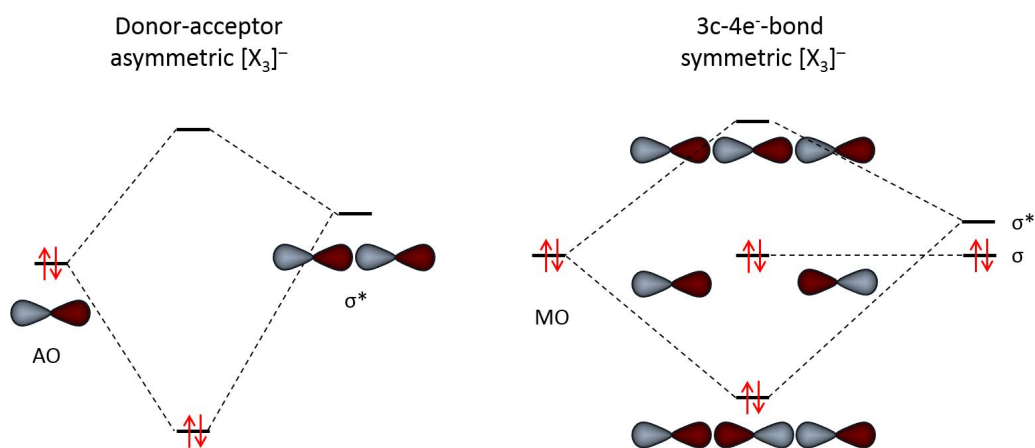


Figure 1. Molecular orbital scheme of a donor-acceptor complex for asymmetric $[X \cdots X-X]^-$ anions (left) and a 3c-4e bonding situation for symmetric $[X_3]^-$ anions (right).^[7] © Wiley-VCH Verlag GmbH & Co. KGaA

The concept of halogen bonding was defined by IUPAC in 2013 and is primarily used to describe electrostatic interactions between halogens and other elements such as oxygen or nitrogen.^[15] According to this concept, the electrostatic potential of a halogen molecule is anisotropic and can be divided into two regions: a belt of higher electron density orthogonal to the molecule's bonding axis, and a region of a more electropositive electrostatic potential on the bonding axis, the so-called σ -hole.^[16] The size of the σ -hole and the tendency to form strong halogen bonds is increasing from fluorine to iodine due to the increasing polarizability, which corresponds with the number of known polyhalogen compounds in the literature.^[7] Symmetric halogens, such as I_2 and Br_2 , have a symmetric σ -hole on both halogen atoms. However, interhalogens or pseudohalogens, such as $BrCl$ or $BrCN$, possess a polarized bond and therefore exhibit a more pronounced σ -hole at the more electropositive halogen atom. Consequently, the σ -hole at the more electronegative side of the molecule is drastically smaller or even negligible, see Figure 2.^[7,17]

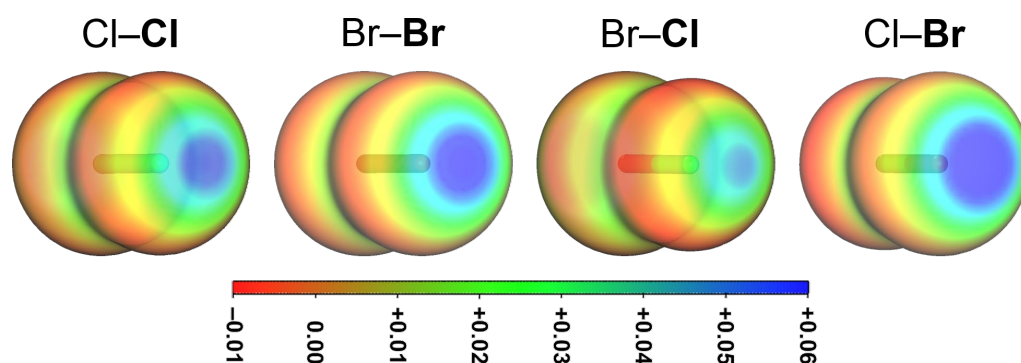


Figure 2. Electrostatic potential of the molecules Cl_2 , Br_2 and $BrCl$ (view of the **Cl** or **Br** atom) in the range of -0.01 a.u. (red) to 0.06 a.u. (blue) mapped onto their electron densities (isosurface value 0.0035 a.u.), calculated at B3LYP-D3(BJ)/def2-TZVPP level of theory.^[17] © 2020 The Authors. Published by Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

The polarized bond combined with the asymmetric σ -holes are reasons for stronger halogen bonding and for the reduced tendency to form polyhalogen networks. This differs significantly from the symmetric halogens and offers advantages for the isolation of discrete polyinterhalogen and polypseudohalogen anions, see section 1.2.

Furthermore, halogen bonding is often compared with hydrogen bonding. Whereas hydrogen bonds can also be very strong (>155 kJ mol^{-1} in $[HF_2]^-$)^[18], halogen bonding covers a wide range and is highly dependent on the electrostatic surrounding (5 kJ mol^{-1} in chlorocarbons, 180 kJ mol^{-1} in $[I_3]^-$)^[19]. Halogen bonds are strongly directional due to interactions with nucleophiles through the σ -hole (180°) and with electrophiles via the more electronegative belt (90°), see Figure 2. The closer the bond angle approaches 90° or 180° , the stronger the halogen bond.^[20]

1.2. Stability of and Influences on Polyhalogen Anions

Polyhalogen monoanions $[X_{2n+1}]^-$ differ in their size, their stability, and their structural motifs. These anions often follow the valence shell electron pair repulsion model (VSEPR), which enables an estimation of the structural motif, see Figure 3. Additionally, the prediction of the structures can be provided by state-of-the-art quantum-chemical calculations.

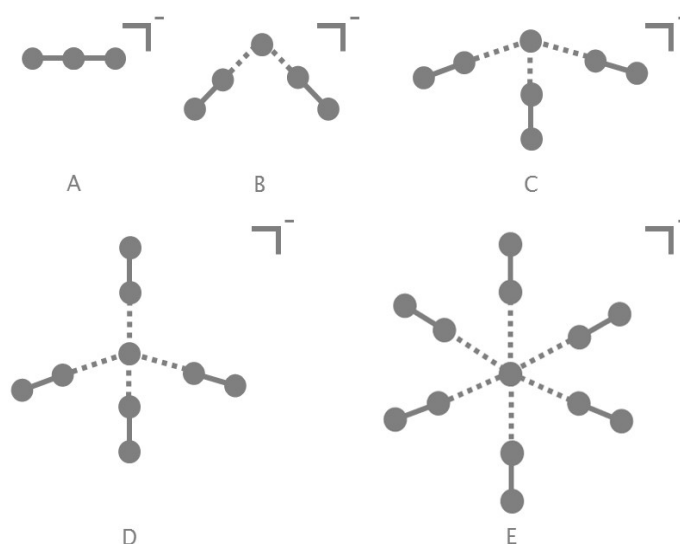


Figure 3. Typical structures of polyhalogen monoanions: A) linear $[X_3]^-$, B) V-shaped $[X_5]^-$, C) trigonal-pyramidal $[X_7]^-$, D) tetrahedral $[X_9]^-$, E) octahedral $[X_{13}]^-$.^[7]
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In general, the most stable polyhalogen monoanion is $[X_3]^-$, which has been reported numerous in the literature.^[7] Larger polyhalogen compounds tend to lose the coordinating X_2 molecules. The higher the coordination number of the central halide, the less charge can be donated into the corresponding LUMO (σ^*) of each coordinating X_2 molecule. This leads to a reduced binding energy and consequently a lower stability of the polyhalogen compound. This agrees with quantum-chemical calculations (SCS-MP2/def2-TZVPP) of the dissociation energies of polyhalogen monoanions $[X_{2n+1}]^-$ ($X = F, Cl, Br, I; n = 1 - 4$), see Table 1.^[7]

Table 1. Dissociation energies [kJ mol^{-1}] for polyhalogen anions calculated at the SCS-MP2/def2-TZVPP level of theory.^[7] [a] values taken from Haller *et al.*^[21]

Reaction	X = F	X = Cl	X = Br ^[a]	X = I ^[a]
$[X_3]^- \rightarrow X_2 + X^-$	110	110	127	132
$[X_5]^- \rightarrow X_2 + [X_3]^-$	12	36	56	67
$[X_7]^- \rightarrow X_2 + [X_5]^-$	12	31	43	60
$[X_9]^- \rightarrow X_2 + [X_7]^-$	6	28	37	47

In addition to the decreasing stability with regard to the increasing size of the polyhalogen anion, another clear trend becomes apparent. The stability of polyhalogen compounds increases in the order $F < Cl < Br < I$, which corresponds with the pronounced σ -hole and the resulting strength of the formed halogen bonds.^[7]

The structural motif of polyhalogen compounds depends heavily on various influences. First, the structure of the anion depends on the choice and the amount of the halogen used. Logically, the probability of obtaining a larger structural motif, such as the tetrahedron, can only be prepared by using a certain amount of halogen. Moreover, some polyhalogen species like polyfluorine monoanions are very unstable (Table 1) and only few have been observed under cryogenic conditions in noble-gas matrices (see section 1.3.1), which makes the stabilization of large polyfluorine anions very unlikely.^[7] In contrast, polyiodine compounds show high stabilities and excellent halogen bonding properties. Nevertheless, they tend to form extended networks rather than discrete anions with specific structural motifs.^[22,23] Due to their polarized bond, interhalogens and pseudohalogens, such as BrCl and BrCN, offer a good compromise between strong halogen bonding properties (pronounced σ -hole) and a reduced tendency to form polyhalogen networks, as illustrated by the electrostatic potentials shown in Figure 4.^[24]

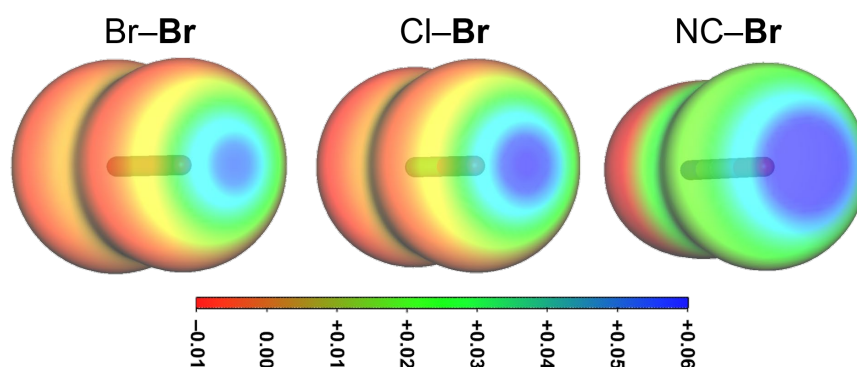


Figure 4. Electrostatic potential of the Br₂, BrCl and BrCN (view of the Br atom) in the range of -0.01 a.u. (red) to 0.06 a.u. (blue) mapped onto their electron densities (isosurface value 0.002 a.u.), calculated at B3LYP-D3/def2-TZVPP level of theory.^[24] © Wiley-VCH Verlag GmbH & Co. KGaA

Consequently, the formation of large and discrete polyinterhalogen and polypseudohalogen species based on BrCN and BrCl should be feasible, as it was already shown by large polyinterhalogen compounds based on other interhalogens, such as [I₄Br₅]⁻.^[8]

In addition to the properties of the halogen, external factors, such as the temperature, the solvent, the counter ion, or weak interactions in the solid state, also have a significant influence on the structural motif of the polyhalogen anion. If a particular structural motif of the

associated polyhalogen anion is to be synthesized, a change in the solvent may play a crucial role. The so far highest polyinterhalogen monoanion in $[\text{NMe}_4][\text{I}_4\text{Br}_5]$ was found in two different structural motifs (for a detailed description of the structures, see section 1.3.4) depending on the solvent, see Figure 5.^[8]

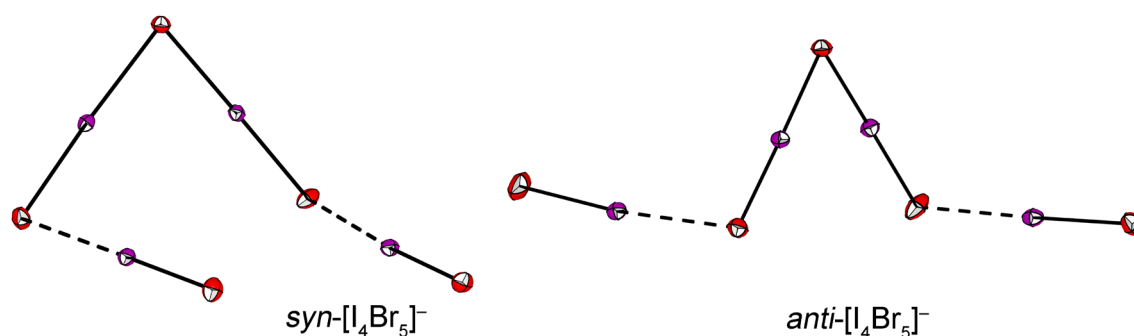


Figure 5. *Syn-* and *anti-*arrangements of the polyinterhalogen monoanions $[\text{I}_4\text{Br}_5]^-$ (red = bromine, purple = iodine) in the solid state structures of $[\text{NMe}_4][\text{I}_4\text{Br}_5]$ crystallized from $[\text{HMIM}]\text{Br}$ (left) and DCM (right).^[7,8] © Wiley-VCH Verlag GmbH & Co. KGaA

When the synthesis was performed in dichloromethane (DCM), single crystals were obtained at $-24\text{ }^\circ\text{C}$ and XRD analysis revealed an *anti*-conformation of the anion. However, using the room-temperature ionic liquid (RT-IL) $[\text{HMIM}]\text{Br}$ (HMIM = 1-hexyl-3-methylimidazolium) as a solvent leads to a crystallization at room temperature and XRD analysis showed a *syn*-conformation of $[\text{I}_4\text{Br}_5]^-$, see Figure 5. Thus, the solvent has a direct influence on the structural motif. Furthermore, some solvents, like ethanol and acetone, cannot be used in the synthesis of polyhalogen anions because they are not stable against side reactions with the halogens.^[25] These problems can be avoided if the synthesis is carried out in ionic liquids, which on the one hand possess a high stability against the strongly oxidizing halogens and on the other hand reduce their volatility (see section 1.4).^[9] Another approach is the synthesis of the desired compound in an excess of the corresponding halogen without another solvent. Both methods made it possible to synthesize and characterize polyhalogen compounds with various structural motifs, such as $[\text{Cl}_8]^{2-}$, $[\text{Cl}_{13}]^-$ and $[\text{Br}_{20}]^{2-}$.^[10,11,26]

Weak interactions in the solid state, such as hydrogen and halogen bonding between cations and anions also have a major influence on the structural motif of the polyhalogen species. Recently, the existence of the free trichlorine monoanion $[\text{Cl}_3]^-$ in solid noble gas matrices under cryogenic conditions was reported.^[27] In the IR spectrum a metal and matrix gas independent band at 252 cm^{-1} was assigned to the asymmetric stretch of free $[\text{Cl}_3]^-$, which is in good agreement with the predicted value (269 cm^{-1} , CCSD(T)/def2-TZVPP). for the calculated minimum structure of the symmetric trichlorine monoanion.^[27]

Figure 6 shows the structure of the calculated, symmetric $[\text{Cl}_3]^-$ compared to the highly asymmetric trichlorine monoanion in $[\text{NMe}_4][\text{Cl}_3]$, highlighting the influences of hydrogen bonding on the structural motif. The bond lengths of the asymmetric trichlorine monoanion, which can be best described as a Cl^- coordinated by one Cl_2 molecule $[\text{Cl}\cdots\text{Cl}_2]^-$, differ by almost 37 pm. This results from multiple hydrogen bonds between the anion and three surrounding cations in the solid. The usually featured 3c-4e bond for symmetric trihalogen species is highly disturbed, which leads to an asymmetric donor-acceptor complex, see Figure 1.^[7]

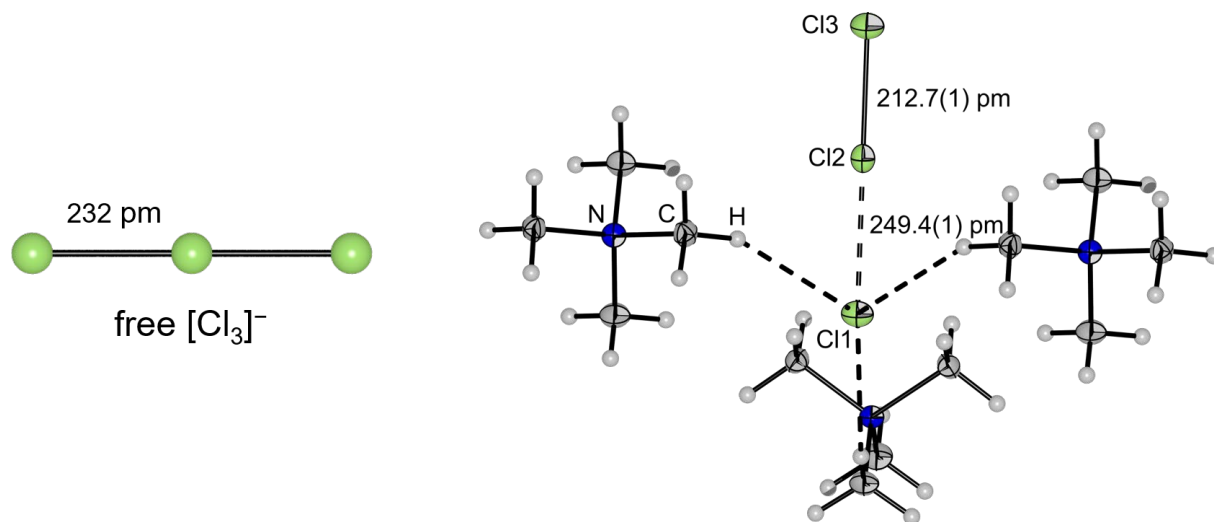


Figure 6. Calculated structure of the free $[\text{Cl}_3]^-$ in $D_{\infty h}$ symmetry (CCSD(T)/def2-TZVPP) and the structure of the asymmetric $[\text{Cl}\cdots\text{Cl}_2]^-$ in the salt $[\text{NMe}_4][\text{Cl}_3]$.^[7,27]

Another example for weak interactions that have a strong influence on the resulting structural motif can be seen in the solid-state structure of $[\text{C}_5\text{H}_{10}\text{N}_2\text{Br}]_2[\text{Br}_6]$.^[28] The structure of the L-shaped dianion consists of two interacting tribromine anions and is calculated to be about 9 kJ mol^{-1} less favorable in energy than the predicted T-shaped minimum structure (RI-MP2/aug-cc-PVTZ, COSMO $\epsilon = 100$). However, this gap in energy may be overcome due to halogen bonding between the dianion and the two cations. The bromine atoms of the two cations interact with the $[\text{Br}_6]^{2-}$ in distances of $345.6(1) \text{ pm}$ and $340.1(1) \text{ pm}$, respectively, which is noticeably below the sum of the van der Waals radii (370 pm), see Figure 7.^[28,29] Consequently, intermolecular halogen-halogen interactions in the solid state have a strong influence on the structural motif of the polyhalogen compounds. This is also proven by the molecular structure in the solid of the interhalogen anion $[\text{Cl}(\text{I}_2)_4]^-$, which shows a square-planar instead of the expected tetrahedral structural motif, see section 1.3.4.^[30]

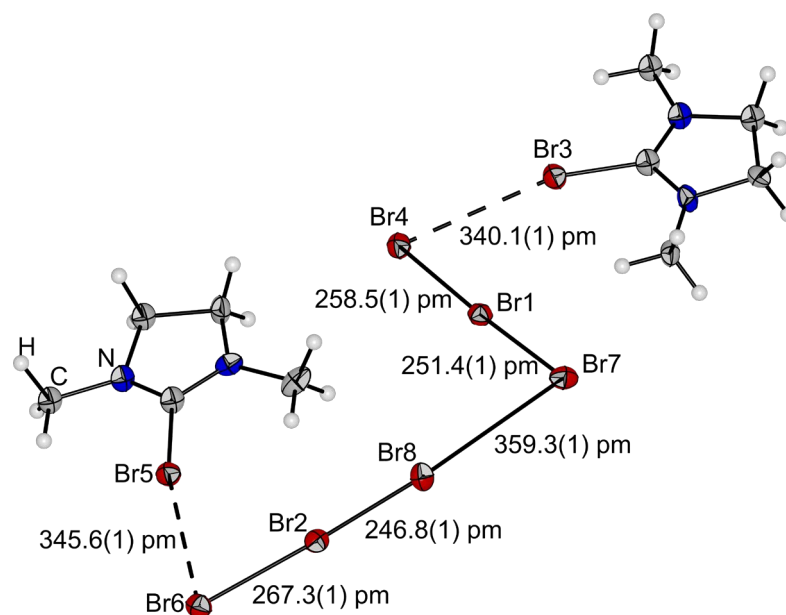


Figure 7. Solid state structure of $[\text{C}_5\text{H}_{10}\text{N}_2\text{Br}]_2[\text{Br}_6]$.^[7,28] © Wiley-VCH Verlag GmbH & Co. KGaA, Reproduced and modified with permission.

The structural motif of the polyhalogen anion can also be influenced by the choice of the counter ion. To obtain suitable single crystals for XRD analysis, highly symmetric cations are more favorable than asymmetric cations. Furthermore, similarly sized cations and anions lead to a denser packing in the solid state and ultimately to an increase in lattice energy. In general, a larger, weakly coordinating cation, such as bis(triphenylphosphine)iminium ($[\text{PNP}]^+$), stabilizes large polyhalogen anions, as it was demonstrated in $[\text{PNP}][\text{Cl}_{13}]$ ^[11] as well as $[\text{PNP}][\text{Br}_{11}]\cdot\text{Br}_2$.^[31] In contrast, smaller, more asymmetric counter ions lead to the formation of ionic liquids, which are thoroughly discussed in section 1.4. Further studies on the influence of the cation on the structural motif of the anion were performed with nonabromine monoanions of the series $[\text{NR}_4][\text{Br}_9]$ ($\text{R} = \text{Me}, \text{Et}, \text{Pr}, \text{Bu}$).^[21] All $[\text{Br}_9]^-$ species were synthesized by adding an excess of eight equivalents of Br_2 to the corresponding bromide salt. However, the resulting solid-state structures differ, going from the most discrete nonabromine anion in $[\text{NPr}_4][\text{Br}_9]$, to extended 3D-networks in $[\text{NMe}_4][\text{Br}_9]$ and $[\text{NEt}_4][\text{Br}_9]$, to a new structural motif, consisting of the building blocks Br^- , $[\text{Br}_3]^-$ and Br_2 , in $[\text{NBu}_4][\text{Br}_9]$.^[21]

If all of these aspects are considered, it becomes clear that there are a number of aspects to consider obtaining a desired polyhalogen anion. Likewise, in addition to the structural diversity (see section 1.3.) we can tune the physico-chemical properties of these compounds in order to expand the potential applications (see section 1.5.) of these systems, e.g. as reactive ionic liquids.

1.3. Structural Diversity of Polyhalogen Anions

Halogens possess rather high electron affinities and ionization potentials and therefore tend to form anions, which in turn can interact attractively with halogen molecules to form polyhalogen anions. This leads to a large structural variety of homoatomic polyhalogen species $[X_n(X_2)_m]^{n-}$ (see Figure 8) and interhalogen compounds $[X_n(Y_2)_m]^{n-}$ or $[X_n(YZ)_m]^{n-}$ ($X, Y, Z = \text{halogen}$).^[7] The number of known polyhalogen anions increases significantly from fluorine to iodine, which is why the vast chemistry of polyiodine compounds, that is subject to detailed reviews^[22,23], is not discussed here. Furthermore, the chemistry of polyhalogen compounds can be expanded by replacing a halogen atom with a pseudohalogen, which resembles the halogens in their chemistry, to obtain less researched polypseudohalogen anions.^[32,33]

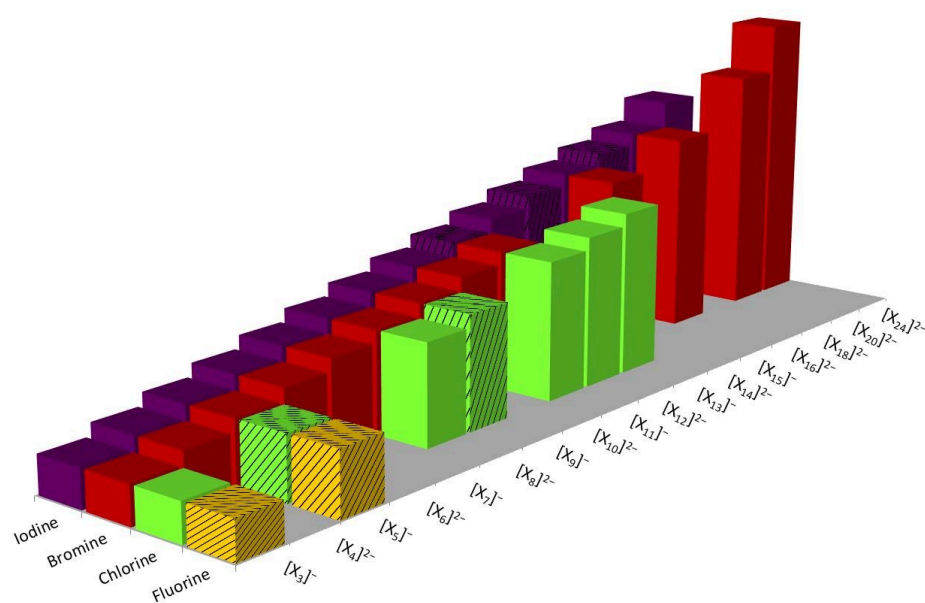


Figure 8. Overview of crystallographically characterized homoatomic polyhalogen mono- and dianions. Shaded bars indicate that these anions have just been observed spectroscopically.^[7] © Wiley-VCH Verlag GmbH & Co. KGaA

1.3.1 Polyfluorine Anions

Fluorine is the most electronegative and reactive element of the periodic table which reacts violently with almost all elements. This can be explained by the relatively low binding energy of the F-F bond, which is why more stable bonds to other elements than fluorine, such as carbon, are energetically favored.^[34] Hence, strict safety precautions and a demanding experimental setup are required when working with elemental fluorine. Therefore, it is not surprising that only two polyfluorine monoanions, the trifluorine monoanion $[\text{F}_3]^-$ and the pentafluorine monoanion $[\text{F}_5]^-$, have been reported so far.^[7]

In the early 1950s, Bode and Klesper postulated the synthesis of trifluorine monoanions after treating alkali metal chlorides with a flow of elemental fluorine and characterized the products via gravimetry, X-ray powder diffraction, and density measurements. However, a structural evidence by single-crystal X-ray diffraction or vibrational spectroscopy was lacking.^[35] In 1961 it was shown that the postulated synthesis led to the formation of alkali fluoridochlorates.^[36] The first spectroscopic evidence of the trifluorine monoanion was reported by Ault and Andrews in 1976. They co-deposited thermally evaporated metal fluorides with a fluorine/argon gas mixture under cryogenic conditions and characterized the formed ion pair complexes MF_3 ($\text{M} = \text{K}, \text{Rb}, \text{Cs}$) by Raman and IR spectroscopy.^[37,38] They observed one symmetric stretching vibration in the Raman spectrum at 460 cm^{-1} ($\nu_s(\text{CsF}_3)$) and one band at 389 cm^{-1} , which was assigned to a higher salt complex of CsF and F_2 . In the IR spectrum, bands at 550 cm^{-1} were assigned to the antisymmetric stretch of MF_3 .^[37,38] In 1999, free $[\text{F}_3]^-$ was observed by mass spectrometry for the first time.^[39] First spectroscopic evidence of the free trifluorine monoanion $[\text{F}_3]^-$ was reported in 2010 after co-deposition of laser-ablated transition metals with fluorine under cryogenic conditions. The IR spectrum in neon shows a metal-independent band at 525 cm^{-1} , which was assigned to the antisymmetric stretching vibration of the isolated $[\text{F}_3]^-$.^[40] Five years later, matrix isolation studies of free $[\text{F}_3]^-$ and its alkali ion pairs was achieved by laser ablation of alkali fluorides. In addition to the IR absorption bands at 561 and 557 cm^{-1} , combination bands ($\nu_s + \nu_{\text{as}}$) of $[\text{F}_3]^-$ and CsF_3 were reported for the first time.^[41]

In 2010 the pentafluorine monoanion $[\text{F}_5]^-$ was calculated to be thermodynamically stable towards the elimination of F_2 with an energy barrier of 18 kJ/mol ($T = 0 \text{ K}$, CCSD(T)/aug-cc-pVTZ). Surprisingly, for its ground state, a “hockey stick” like structure was calculated to be

6.2 kJ/mol more stable than the V-shaped C_{2v} transition state (Figure 9).^[40] After co-deposition of laser-ablated transition metals with F_2 under cryogenic conditions, first spectroscopic validation of the free $[F_5]^-$ was obtained in 2015. A metal independent band at 850 cm^{-1} was found in the IR spectrum and assigned to the antisymmetric stretch of $[F_5]^-$.^[41,42] The experimental results support the V-shaped structure and contradict the calculations, which predicted a “hockey stick” structure with, at least, two F-F stretching vibrations. This dissent is still topic of ongoing research and high-level quantum-chemical calculations.

Polyfluorine anions with a higher fluorine content than in $[F_5]^-$ have not been reported experimentally, but are subject of theoretical studies.^[43] Furthermore, attempts to synthesize and isolate polyfluorine compounds in bulk have not been successful so far.

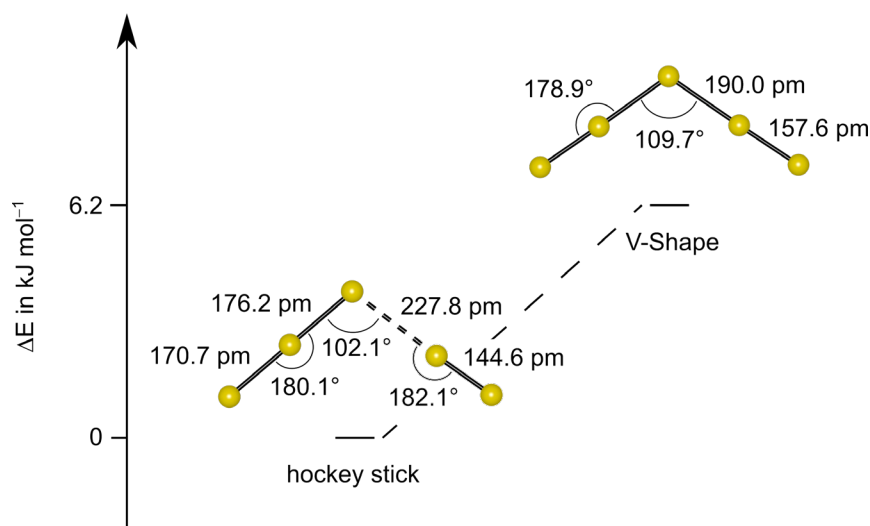


Figure 9. “Hockey stick” like ground state and first-order transition state (V-shaped) of the $[F_5]^-$ monoanion; calculated at CCSD(T)/aug-cc-pVTZ level of theory.^[7,40] © Wiley-VCH Verlag GmbH & Co. KGaA

1.3.2 Polychlorine Anions

Due to stronger halogen bonding and reduced reactivity of Cl_2 compared to F_2 , more polychlorine anions have been reported than polyfluorine anions. Thus far, the four polychlorine monoanions $[\text{Cl}_3]^-$, $[\text{Cl}_5]^-$, $[\text{Cl}_{11}]^-$ and $[\text{Cl}_{13}]^-$ as well as the dianions $[\text{Cl}_8]^{2-}$ and $[\text{Cl}_{12}]^{2-}$ have been synthesized and crystallographically characterized. Furthermore, $[\text{Cl}_9]^-$ has been observed spectroscopically.^[7]

It took more than forty years after the first discovery of trihalogen species by Chattaway and Hoyle in 1923^[6] until vibrational spectra confirmed the existence of $[\text{NR}_4][\text{Cl}_3]$ ($\text{R} = \text{Et}, \text{Pr}, \text{Bu}$).^[44] About ten years later, matrix-isolation experiments of trichlorine compounds showed two stretching modes in the IR spectrum, which indicated an asymmetric structure of $[\text{Cl}_3]^-$.^[45] This nearly linear but slightly asymmetric structure of trichlorine monoanions has thus far been found in all structures obtained by single-crystal X-ray diffraction. This can be explained by solid state interactions between the anion and the cation such as hydrogen or halogen bonding (see section 1.2.). Recently, the existence of free linear trichlorine monoanions was observed after salt ablation of alkali metal chlorides and Cl_2 under cryogenic conditions.^[27] The first crystallographic proof of a trichlorine anion was reported by Bogaard and co-workers in 1981.^[46] They obtained the $[\text{Cl}_3]^-$ salt after diffusion of elemental Cl_2 through an aqueous solution of tetraphenylarsonium chloride and observed discrete anions in the solid, which are arranged in zigzag chains. In the following decades only a few more solid-state structures of $[\text{Cl}_3]^-$ with different cations were published, but none of them possessed a completely symmetric structure.^[47]

The pentachlorine monoanion $[\text{Cl}_5]^-$ was mentioned for the first time in 1966 as Evans and Lo added Cl_2 to a solution of tetraalkylammonium chloride in acetonitrile.^[44] The Raman spectrum showed a broad band at 482 cm^{-1} , which could neither be assigned to elemental Cl_2 nor to a $[\text{Cl}_3]^-$. After increasing the amount of Cl_2 to an excess ratio of 3:1, the previously observed band for the trichlorine monoanion at 275 cm^{-1} vanished and only two bands at 482 and 538 cm^{-1} ($\nu \text{ Cl}_{2(\text{t})}$)^[48] remained. The formation of an L-shaped pentachlorine monoanion was suggested by the authors, since this structural motif was already known from the pentaiodine monoanion $[\text{I}_5]^-$.^[49] This first evidence for a $[\text{Cl}_5]^-$ was confirmed by Taraba and Zak in 2003, as they reacted $[\text{PPh}_2\text{Cl}_2][\text{Cl}_3]$ with an excess of Cl_2 and observed almost the same Raman bands

as Evans and Lo.^[50] Besides the spectroscopic results, Taraba and Zak obtained yellow single crystals, which were suitable for single-crystal X-ray diffraction analysis.

The observed L-shaped structure (“hockey stick”) of the pentachlorine monoanion in $[\text{PPh}_2\text{Cl}_2][\text{Cl}_3\cdots\text{Cl}_2]$, which was already discussed for the $[\text{F}_5]^-$ anion (see section 1.3.1), consists of a very asymmetric $[\text{Cl}_3]^-$ (241.9(2) and 214.4(2) pm) and a coordinating Cl_2 molecule, see Figure 10.^[50]

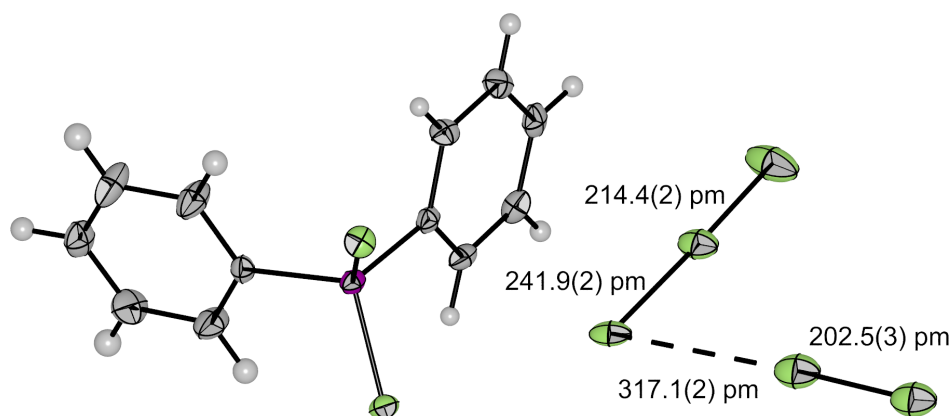


Figure 10. Molecular structure in the solid of the salt $[\text{PPh}_2\text{Cl}_2][\text{Cl}_3\cdots\text{Cl}_2]$.^[7,50] © Wiley-VCH Verlag GmbH & Co. KGaA

The distance between the $[\text{Cl}_3]^-$ and the Cl_2 moiety is 317.1(2) pm, which is significantly shorter than the sum of the van-der-Waals radii of chlorine (350 pm)^[29] and justifies the description of the ion as a $[\text{Cl}_5]^-$. Quantum-chemical calculations (CCSD(T)/aug-cc-pVTZ) predicted a V-shaped minimum structure for the $[\text{Cl}_5]^-$ in C_{2v} symmetry. The calculated $[\text{Cl}_5]^-$ consists of a central chloride, which is coordinated by two Cl_2 molecules at a distance of 254.3 pm.^[51,52] This indicates again that the choice of the cation and interactions in the solid state have a great influence on the structure of the anion.

The heptachlorine as well as the nonachlorine monoanion, $[\text{Cl}_7]^-$ and $[\text{Cl}_9]^-$, have so far only been investigated by quantum-chemical calculations and vibrational spectroscopy. The calculations predict endothermic decomposition reaction (loss of Cl_2) for both anionic species. In case of the heptachlorine monoanion, a trigonal-pyramidal structure, which consists of a central Cl^- , which is surrounded by three Cl_2 molecules, is calculated to be the energetic minimum.^[51] In 2012, first Raman spectroscopic evidence for a nonachlorine monoanion was found after condensing an excess of Cl_2 onto $[\text{NEt}_4]\text{Cl}$.^[51] In the Raman spectrum, two bands at 460 and 430 cm^{-1} were observed and assigned to the $[\text{Cl}_9]^-$. Those bands were validated by quantum-chemical calculations (RI-MP2/def2-TZVPP), which predicted a tetrahedral

minimum structure and Raman bands at 473 and 435 cm^{-1} , respectively.^[51] This structural motif is in accordance with the already literature known nonabromine monoanion $[\text{Br}_9]^-$.^[12] In 2018, two large polychlorine monoanions were added to the list of structurally characterized polychlorine compounds.^[11] The undecachlorine monoanion $[\text{Cl}_{11}]^-$ exists in both, a monomeric form in $[\text{PNP}][\text{Cl}_{11}]\cdot\text{Cl}_2$, and in one-dimensional chains, as in $[\text{PPh}_4][\text{Cl}_{11}]$ and $[\text{AsPh}_4][\text{Cl}_{11}]$. While the monomeric form can be best described as a distorted square-pyramidal structure with an additional embedded Cl_2 molecule, the chains consist of interconnected $[\text{Cl}_{11}]^-$ units.^[11] Condensing an excess of chlorine onto $[\text{PNP}]\text{Cl}$ in acetonitrile resulted in the formation of the tridecachlorine monoanion $[\text{Cl}_{13}]^-$. The $[\text{Cl}_{13}]^-$ anion consists of a central chloride ion, which is coordinated by six Cl_2 molecules in a distorted octahedral geometry. The anions are interconnected with a distance of 328.7(1) pm, which is about 21 pm shorter than the sum of the van-der-Waals radii, to form a chain, see Figure 11.^[11]

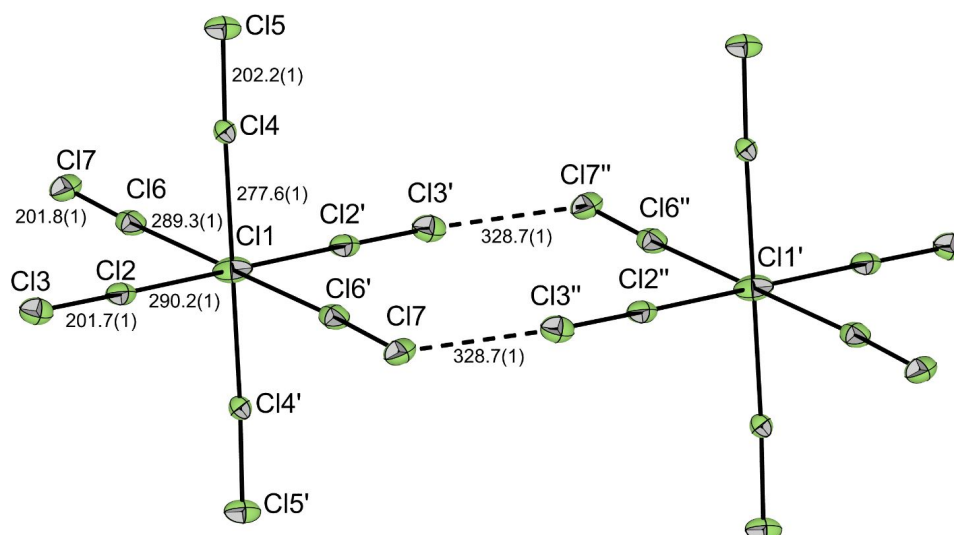


Figure 11. Interactions between the $[\text{Cl}_{13}]^-$ monoanions forming a chain in the solid-state structure of $[\text{PNP}][\text{Cl}_{13}]$. Bond lengths given in pm.^[11] © Wiley-VCH Verlag GmbH & Co. KGaA

Besides the monoanions, two polychlorine dianions were reported so far. The octachlorine dianion $[\text{Cl}_8]^{2-}$ was synthesized with the cation $[\text{CCl}(\text{NMe}_2)_2]^+$ in the ionic liquid $[\text{BMP}][\text{OTf}]$ and characterized via Raman spectroscopy and XRD.^[10] Its Z-shaped structure is similar to the heavier homologues $[\text{Br}_8]^{2-}$ ^[53,54] and $[\text{I}_8]^{2-}$ ^[55], and can be either described as two distorted $[\text{Cl}_3]^-$ units bridged by a Cl_2 molecule or as $[\text{Cl}_2\text{-Cl-Cl}_2\text{-Cl-Cl}_2]$.^[10] A comparable structural motif was found in a two-dimensional, infinite polychlorine network. In comparison to the $[\text{Cl}_8]^{2-}$ dianions, which can be considered as isolated dianions in the solid, the 2D structural network is held together by halogen-halogen bonding and solid state interactions.^[56]

The dodecachlorine dianion $[\text{Cl}_{12}]^{2-}$ is the highest known polychlorine dianion so far and was reported in 2018. Its molecular structure in the solid state consists of two pentachlorine monoanions, which are bridged by a Cl_2 molecule, see Figure 12. In the crystal, the dianions are arranged in a three-dimensional network, which resembles honeycomb pattern. The resulting voids are occupied by the $[\text{NMe}_3\text{Ph}]^+$ cations.^[11]

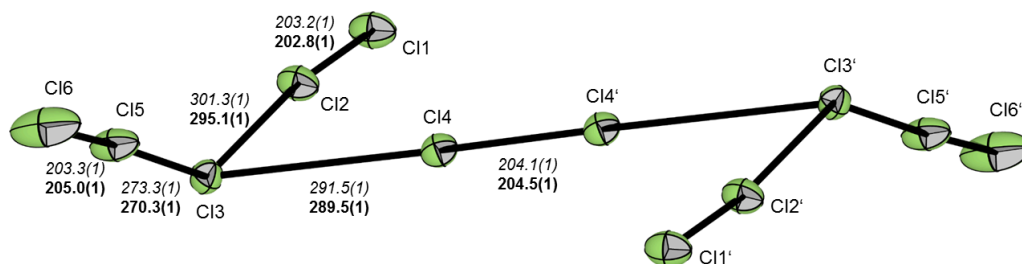


Figure 12. Solid state structure of the dianion $[\text{Cl}_{12}]^{2-}$ in $[\text{NMe}_3\text{Ph}]_2[\text{Cl}_{12}]$. Bond lengths in pm are given for the two crystallographically independent dianions in **bold** and *italics*, respectively.^[11]
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1.3.3 Polybromine Anions

Compared to the rather rare polyfluorine and polychlorine anions, the variety of reported polybromine anions is significantly higher. On the one hand, this can be explained by the liquid aggregate state of Br_2 , which makes syntheses of polybromine species much more accessible than the use of gaseous Cl_2 and especially F_2 . On the other hand, Br_2 possesses a more distinct σ -hole and can be polarized more easily than the lighter homologues Cl_2 and F_2 , which results in stronger halogen bonding and eventually in the formation of polybromine anions. Because of the latter properties, polybromine species also tend to form extensive networks and not just discrete anions. Thus far, five polybromine monoanions from $[\text{Br}_3]^-$ to $[\text{Br}_{11}]^-$ as well as eight polybromine dianions from $[\text{Br}_4]^{2-}$ to $[\text{Br}_{24}]^{2-}$ were structurally characterized.^[7]

As expected, the tribromine monoanion $[\text{Br}_3]^-$ has been investigated most thoroughly. The symmetry or asymmetry of the tribromine anion, as already described for the $[\text{Cl}_3]^-$, depends on the interactions with the cations or neighboring anions in the solid. In 2011, high-quality solid state structural data ($R_1 \leq 0.05$) of tribromine monoanions were studied by Pichierri, which show that approximately one fourth of the anions are symmetric.^[57] Those results were updated recently, resulting in a plot of 101 $[\text{Br}_3]^-$ structures (Figure 13).^[7]

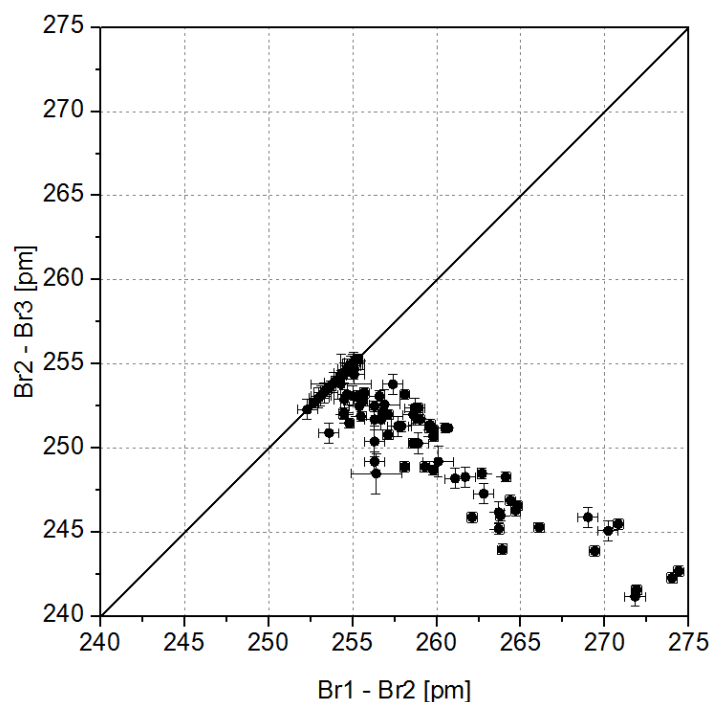


Figure 13. Plot of the Br-Br bond lengths of 101 known $[\text{Br}_3]^-$ solid state structures (CCDC; $R_1 \leq 0.05$). Error bars represent the 3σ range of uncertainty.^[7] © Wiley-VCH Verlag GmbH & Co. KGaA

The pentabromine monoanion $[\text{Br}_5]^-$ was spectroscopically observed for the first time in 1967 by Evans and Lo as they added two equivalents of Br_2 to a potassium bromide solution and observed a new band at 250 cm^{-1} in the Raman spectrum.^[58] The assumed V-shaped molecule was structurally confirmed 45 years later and consists of a central Br^- , which is coordinated by two Br_2 units. The bond lengths of the coordinating Br_2 molecules (241.3(1), 240.6(1) pm) are significantly elongated in comparison to free Br_2 (229 pm)^[59] in the solid state due to charge transfer from the HOMO of the Br^- to the LUMO of the coordinating Br_2 molecules, see section 1.1.^[60]

Quantum-chemical calculations and first spectroscopic evidence of the heptabromine monoanion $[\text{Br}_7]^-$ suggested a trigonal pyramidal structure in C_{3v} symmetry.^[61] Crystallographic proof was provided only a little later by Feldmann and co-workers after they synthesized $[\text{PPh}_3\text{Br}][\text{Br}_7]$ in an eutectic mixture of the two ILs 1-decyl-1-methylpyrrolidinium bromide and 1-butyl-1-methylpyrrolidinium triflate, and obtained single crystals suitable for XRD-analysis. As expected, they observed a trigonal pyramidal structure, consisting of a central Br^- surrounded by three Br_2 molecules.^[26]

First structural evidence for the next highest polybromine monoanion, the $[\text{Br}_9]^-$, was reported by Haller *et al.* in 2011.^[12] Studies on the influence of the type of tetraalkylammonium cation ($[\text{NR}_4]^+$; R = Me, Et, Pr, Bu) on the structure of the nonabromine anion showed that the most discrete anions are obtained with the cation $[\text{NPr}_4]^+$ as counterion, see Figure 14.^[21]

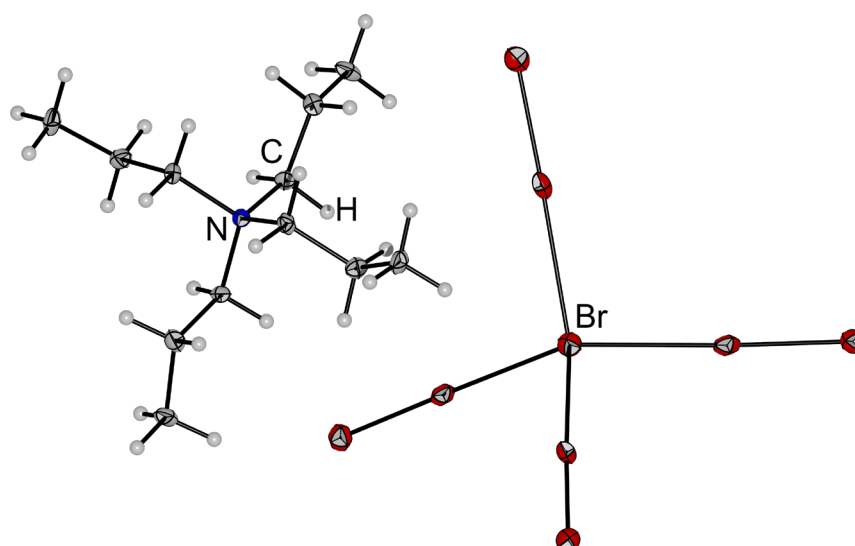


Figure 14. Molecular structure in the solid state of the salt $[\text{NPr}_4][\text{Br}_9]$.^[21]

The nonabromine monoanion can be best described as a central Br^- that is coordinated by four Br_2 molecules in a slightly distorted tetrahedral structure. This is in good agreement with

quantum-chemical calculations, which also predict a tetrahedral ground state.^[12] Electrochemical characterizations of nonabromine compounds revealed a surprisingly high conductivity. Therefore, polybromine species qualify as interesting and promising compounds in electrochemical applications, see section 1.5.

The undecabromine monoanion $[\text{Br}_{11}]^-$ was structurally described for the first time in 2013 and is the highest known polybromine monoanion so far.^[31] The monoanion was isolated with the sterically demanding $[\text{PNP}]^+$ (bis(triphenylphosphine)iminium) cation as $[\text{PNP}][\text{Br}_{11}]\cdot\text{Br}_2$ and consists of a central Br^- that is coordinated in a distorted square pyramidal coordination sphere by five Br_2 molecules, which is also indicated by the calculated Addison geometric parameter ($\tau = 0.18$)^[62]. Moreover, an additional Br_2 co-crystallized within the crystal lattice and the monoanions are loosely interconnected forming a three-dimensional network.^[31]

Quantum-chemical calculations suggest that the highest experimentally stabilizable polybromine monoanion is not the $[\text{Br}_{11}]^-$ but the tridecabromine monoanion $[\text{Br}_{13}]^-$.^[63] The $[\text{Br}_{13}]^-$ should have an octahedral structure as it was already observed for the $[\text{Cl}_{13}]^-$.^[11] However, no clear spectroscopic or structural evidence for the tridecabromine monoanion has been found to date.

The smallest polybromine dianion, the $[\text{Br}_4]^{2-}$, was already structurally characterized in 1959. The anion was synthesized by adding a chloroform solution of Br_2 to dimethylammonium bromide. XRD analysis showed an almost linear structure of the dianion with an angle of approximately 173° .^[64]

The L-shaped hexabromine dianion $[\text{Br}_6]^{2-}$ was reported recently in the structure $[\text{C}_5\text{H}_{10}\text{N}_2\text{Br}]_2[\text{Br}_6]$. It can be best described as two end-on connected tribromine monoanions. The bonding angle between both $[\text{Br}_3]^-$ units is almost perpendicular (87°). This contradicts quantum-chemical calculations that predict a T-shaped minimum structure, but is explained by steric hindrance, as well as halogen-halogen interaction between cation and anion, see Figure 7.^[28] Compared to the only known $[\text{Br}_6]^{2-}$ species, more than a few octabromine dianions are reported in the literature, which all possess a Z-shaped structure that consists of the building blocks $[\text{Br}_3]^-$ and Br_2 . The first $[\text{Br}_8]^{2-}$ was already discovered in 1997.^[54] In the following years, several $[\text{Br}_8]^{2-}$ containing compounds with different counterions or synthetic methods were published.^[26,53,65] Due to the already discussed excellent halogen bonding properties of Br_2 and its enhanced tendency to form extended networks, five polybromine dianions beyond $[\text{Br}_8]^{2-}$ are known to the literature. These anions include the rectangular

decabromine dianion^[66] and the tetradecabromine dianion $[\text{Br}_{14}]^{2-}$ for which two very different structures are known. On the one hand the dianion in the compound $[(\text{C}_6\text{H}_5)_3\text{PBr}]_2[\text{Br}_{14}]$ consists of two connected $[\text{Br}_7]^-$ subunits.^[26] On the other hand the structure of the complex 3D network in $[(\text{C}_6\text{H}_4\text{F})_3\text{PBr}]_2[\text{Br}_{14}]$ can be described as octahedrally coordinated $[\text{Br}_9\text{Br}_2]^-$ units, that are connected with additional $[\text{Br}_3]^-$ molecules.^[67] Furthermore, the sedecabromine dianion $[\text{Br}_{16}]^{2-}$ was discussed for the first time in 2014 and is made of two T-shaped $[\text{Br}_7]^-$ units that are interconnected via a Br_2 moiety.^[68] Another $[\text{Br}_{16}]^{2-}$ was reported recently after the successful stabilization with partially fluorinated cations.^[67] After the large polybromine dianion $[\text{Br}_{20}]^{2-}$ was already reported in 2011^[69], the so far highest polybromine dianion, the tetracosabromine dianion $[\text{Br}_{24}]^{2-}$, was synthesized and characterized in 2015.^[70] The structure of the $[\text{Br}_{24}]^{2-}$ consists of a central Br^- that is coordinated by five Br_2 molecules and an extra end-on coordinated Br_2 unit. The anions are interconnected forming a large 3D network, which is additionally stabilized by twelve $\text{H}\cdots\text{Br}$ contacts.^[70]

1.3.4 Polyinterhalogen Anions

Because of the variety of possible combinations between the halogens, the theoretical number of polyinterhalogen anions is considerably higher than the number of homonuclear polyhalogen compounds. Similar to polyhalogen chemistry, the polyinterhalogen anions of the lighter interhalogens are less explored. This includes, for example, compounds based on the coordination of interhalogens such as BrCl and ClF.^[7]

Generally, polyinterhalogen anions can be divided into two subcategories. Whereas classical polyinterhalogen anions are built of an electropositive center, which is surrounded by more electronegative halogen atoms, non-classical polyinterhalogen anions can be described as a central halide ion X^- that is coordinated by halogen Y_2 or interhalogen molecules XY/YZ , see Figure 15. However, this differentiation is questionable for triatomic polyinterhalogen anions, which have been discussed in extensive reviews of both, classical^[71] and non-classical polyinterhalogen anions.^[7,63] Therefore, this section focuses only on the structural diversity of the larger polyinterhalogen anions.

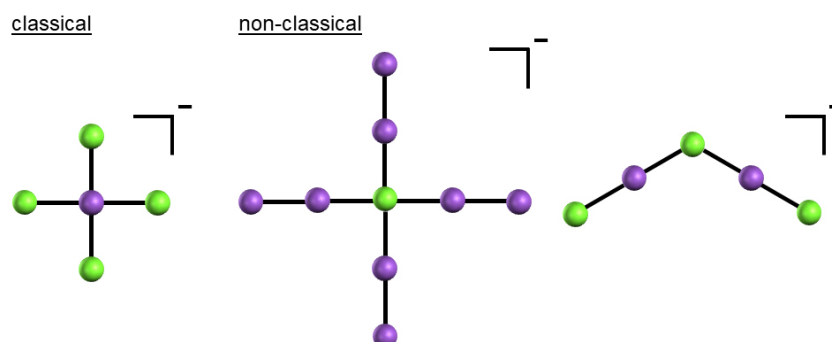


Figure 15. Classical (left) and non-classical polyinterhalogen monoanions (right). The more electropositive atom is depicted in violet, the more electronegative atom in green.^[7] © Wiley-VCH Verlag GmbH & Co. KGaA

The classical polyinterhalogen anion $[\text{BrF}_6]^-$ in $\text{Cs}[\text{BrF}_6]$ was synthesized and characterized by Seppelt and co-workers in 1989.^[72] The structure of the monoanion does not follow the VSEPR model, as is common for poly(inter)halogen compounds, and possesses an octahedral coordination sphere in the solid state as well as in solution.^[72,73] The authors noted that the observed symmetry can neither be explained by crystal lattice forces, nor by steric reasons. The deviation from the VSEPR model may be explained by the s-electrons of bromine, which are strongly bound to the nucleus due to incomplete shielding of the nucleus, caused by the first filled d-shell. As a result, the Br-F bond would be expected to show mainly p-character.^[72] Based on these findings, the structure of the valence isoelectronic $[\text{IF}_6]^-$ monoanion should not be octahedral. This was proven a little later by the solid state structure of $[\text{IF}_6]^-$, which shows

a strongly distorted octahedral structure with almost C_{3v} symmetry.^[74] Crystallographic evidence for the square planar $[\text{BrF}_4]^-$ monoanion was reported in 2013,^[75] after it was characterized spectroscopically in 1970.^[76] The valence isoelectronic classical pentainterhalogen monoanion $[\text{ClF}_4]^-$ has been investigated thoroughly both, spectroscopically^[77,78] and structurally,^[78,79] and also possesses the expected square-planar structure in D_{4h} symmetry. Recently, a new synthetic approach to obtain an organo-soluble $[\text{NEt}_3\text{Me}][\text{ClF}_4]$ salt without the use of the gaseous and highly reactive ClF_3 as starting material was introduced. Additionally, the intermediate $[\text{ClF}_2]^-$ was structurally characterized for the first time and potential application possibilities for these compounds were presented.^[80]

In 2013, the solid state structure of the salt $[(\text{H}_5\text{O}_2)(\text{I}_2\text{b15c5})_2][\text{Cl}(\text{I}_2)_4]$ ($\text{I}_2\text{b15c5}$ = diiodobenzo-15-crown-5) was reported and is an example of both, non-classical interhalogen anions, and the concept of halogen bonding.^[30] The anion consists of a central Cl^- that is coordinated by four I_2 molecules. Surprisingly, the anion possesses a square-planar structure in the solid state in contrast to the known tetrahedral nonabromine monoanion $[\text{Br}_9]^-$.^[12] Quantum-chemical calculations (SCS-MP2/def2-TZVPP) showed that the square-planar structure is 8 kJ mol^{-1} higher in energy than the tetrahedral ground state. However, this energy difference can be overcome by interactions in the solid state. Calculations of the electrostatic potential show halogen bonding between the σ -holes of the peripheral iodine atoms and the lateral belt of the iodine atom of the adjacent molecule (Figure 16), which lead to a gain of energy and stabilize the structural motif.^[30]

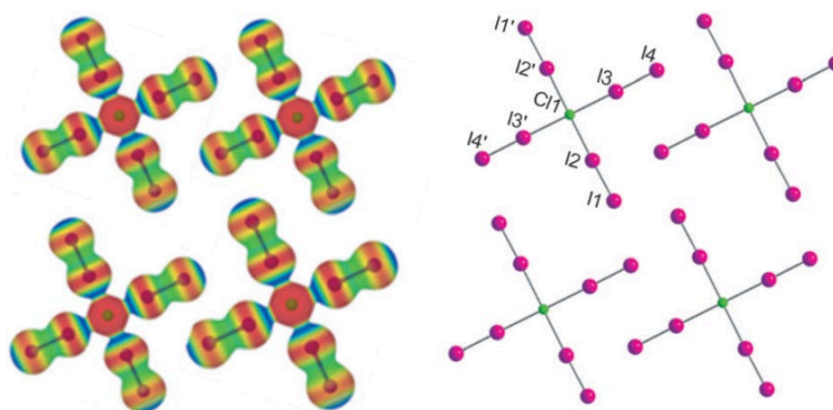


Figure 16. Halogen bonding between the $[\text{Cl}(\text{I}_2)_4]^-$ anions in the solid state indicated by the electrostatic potential.^[30] © Wiley-VCH Verlag GmbH & Co. KGaA

Feldmann and co-workers reported on the compound $[\text{PPh}_3\text{Cl}]_2[\text{Cl}_2\text{I}_{14}]$ as the first polyiodine chloride 3D network. The network, which was synthesized in an IL, is built of distorted square-pyramidal $[\text{Cl}(\text{I}_2)_5]^-$ units, which are interconnected via embedded I_2 molecules.^[26]

In addition to the described polyinterhalogen compounds, which consist of a halide surrounded by symmetric halogens, the central halide can also be coordinated by asymmetric interhalogens such as IBr and ICl. The first non-classical pentainterhalogen monoanion based on ICl was already described in 1942^[81] and spectroscopically characterized 25 years later.^[82,83] Structural evidence for the V-shaped polyinterhalogen monoanion $[\text{Cl}(\text{ICl})_2]^-$ was provided shortly afterwards by Parlow and Hartl.^[84] With the compound $[\text{PPh}_4][\text{Cl}(\text{ICl})_3]$ the next higher polyinterhalogen anion was obtained by the reaction of $[\text{PPh}_4]\text{Cl}$ and ICl. Two different structural motifs, depending on the ratio of the reactants, were characterized. A trigonal-pyramidal (1:3) or a chain-like structure (1:5) were obtained. Quantum-chemical calculations (SCS-MP2/def2-TZVPP) for both structures revealed, that the trigonal-pyramidal structure in C_{3v} symmetry is just 5.1 kJ mol^{-1} more favorable in energy than the chain-like structure in C_{2v} symmetry.^[85] As described for the ICl based compounds, polyinterhalogen anions consisting of a central Br^- with coordinating IBr molecules have also been reported. This includes the V-shaped pentainterhalogen monoanion $[\text{Br}(\text{IBr})_2]^-$,^[86] as well as the heptainterhalogen anion $[\text{Br}(\text{IBr})_3]^-$, which was structurally characterized both as a trigonal-pyramidal^[87] and a planar species.^[88] A different structural motif of a heptainterhalogen anion was reported in $[\text{NEt}_4][\text{I}_5\text{Br}_2]$, after reaction of $[\text{NEt}_4]\text{Br}$ and IBr in the IL $[\text{HMIM}]\text{Br}$, see Figure 17.^[85]

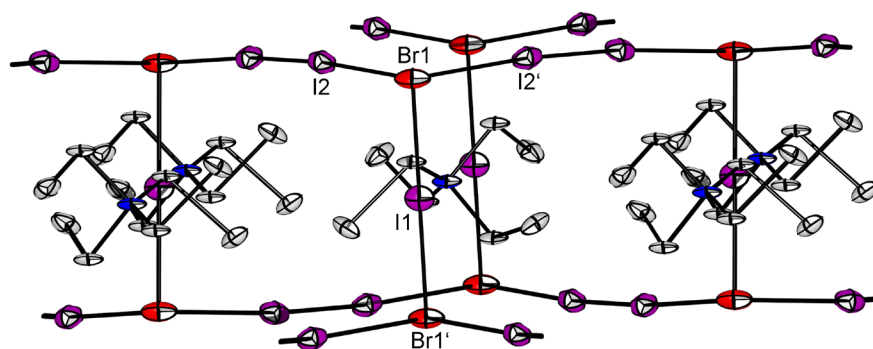


Figure 17. The network of $[\text{I}_5\text{Br}_2]^-$ with the cations situated in between the anionic layers in the solid-state structure of $[\text{NEt}_4][\text{I}_5\text{Br}_2]$.^[7,85] © Wiley-VCH Verlag GmbH & Co. KGaA

The anionic structure consists of symmetric $[\text{Br-I-Br}]^-$ units that are interconnected via two surrounding I_2 molecules at each bromine atom, forming a double layer of Br-I-I-Br-I-I zigzag chains, see Figure 17.^[85] The currently highest polyinterhalogen compound based on IBr is the nonainterhalogen monoanion $[\text{I}_4\text{Br}_5]^-$ in $[\text{NMe}_4][\text{I}_4\text{Br}_5]$.^[8] The anion varies from the usual tetrahedral structure of a nonahalogen monoanion like $[\text{Br}_9]^-$,^[12] and can be synthesized in two different modifications by changing the solvent. Both structures consist of a V-shaped pentainterhalogen monoanion $[\text{Br}(\text{IBr})_2]^-$ that is coordinated by two additional IBr molecules

via the terminal bromine atoms. Synthesis of $[\text{NMe}_4][\text{I}_4\text{Br}_5]$ in the RT-IL $[\text{HMIM}]\text{Br}$ leads to the formation of the *syn*-conformation, in which both IBr molecules point into the same direction, whereas the use of dichloromethane (DCM) as solvent results in the *anti*-conformation with opposing IBr molecules, see chapter 1.2., Figure 5.^[8]

The large number of polyinterhalogen compounds based on IBr and ICl implies that it should also be possible to obtain polyinterhalogen monoanions based on BrCl . Remarkably, only the triinterhalogen monoanion $[\text{Cl-Br-Cl}]^-$ has been reported so far.^[89] A special case that extends the already mentioned definition of non-classical polyinterhalogen anions are compounds, which are built of a central halide that is surrounded by tetraatomic interhalogen molecules, such as BrF_3 . The monoanion $[\text{Br}_2\text{F}_7]^-$ was spectroscopically observed for the first time in 1976.^[90] Structural evidence was provided by Kraus and co-workers in 2013 as they reported the molecular structure of $\text{Cs}[\text{Br}_2\text{F}_7]$ in the solid state, which was followed by the first stabilization of this anion by a p-block element in $[\text{PbF}][\text{Br}_2\text{F}_7]$.^[75,91] $[\text{Br}_2\text{F}_7]^-$ consists of a central F^- , which bridges the bromine atoms of the two BrF_3 molecules, and can be described as $[\text{F}(\text{BrF}_3)_2]^-$.^[75] Three years later, the structure of the polyinterhalogen monoanion $[\text{Br}_3\text{F}_{10}]^-$ was characterized crystallographically. The anion of the compound $\text{Rb}[\text{Br}_3\text{F}_{10}]$ is built of a μ_3 -bridging fluorine ion that is surrounded by three BrF_3 molecules ($[\text{F}(\text{BrF}_3)_3]^-$), see Figure 18.^[92]

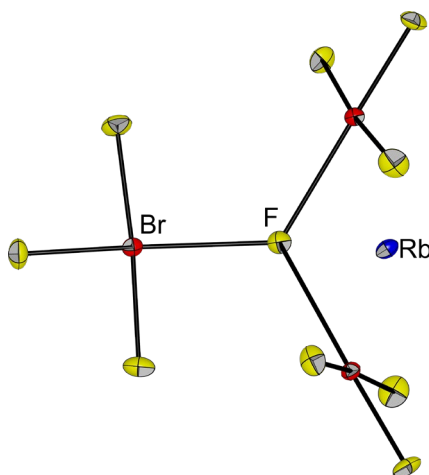


Figure 18. Molecular structure in the solid state of $\text{Rb}[\text{Br}_3\text{F}_{10}]$.^[92]

In addition to the variety of polyinterhalogen monoanions, several polyinterhalogen dianions are known in the literature. The dianion $[\text{I}_2\text{Cl}_2]^{2-}$ was reported in 2008 after reaction of elemental iodine and 2-pyrimidone hydrochloride in DCM/MeOH. The almost linear structure was determined by XRD measurements and can be best described as $[\text{Cl-I-I-Cl}]^{2-}$.^[93] Via a different synthetic approach, the dianions $[\text{Cl-I-I-Cl}]^{2-}$ and $[\text{Br-I-I-Br}]^{2-}$ were obtained after heating of $[\text{HMET}][\text{I}_2\text{Cl}_2]$ and $[\text{HMET}][\text{I}_2\text{Br}_2]$ (HMET = 1,6-bis(trimethylammonium)hexane),

respectively.^[94] A common structural motif for polyinterhalogen dianions is the Z-shaped octainterhalogen dianion that can be compared to the known octahalogen dianions $[\text{Cl}_8]^{2-}$ ^[10] and $[\text{Br}_8]^{2-}$.^[54] The Z-shaped structures consist of two triinterhalogen monoanions that are interconnected via a halogen or interhalogen molecule. Due to the large variation possibilities of the trihalogen anions and the bridging (inter)halogen units, numerous octainterhalogen dianion are known.^[85,95–99] Recently, Z-shaped dianions, which consist exclusively of the halogens Br and Cl, were reported for the first time. The dodecainterhalogen dianion is contained in the compounds $[\text{PPh}_4]_2[\text{I}_6\text{Cl}_6]$ ^[85] and $[\text{PBr}_4]_2[\text{I}_5\text{Br}_7]$.^[100] Both dianions are built of two V-shaped pentainterhalogen monoanions ($[\text{Cl}(\text{ICl})_2]^-$ or $[\text{Br}(\text{IBr})_2]^-$) that are interconnected via an I_2 or IBr molecule, respectively.^[85,100]

The theoretical number of polyinterhalogen anions exceeds the number of homonuclear polyhalogen anions. Nevertheless, the variety of experimentally characterized compounds, especially the polyinterhalogen anions based on lighter interhalogens, such as BrCl , is relatively small and requires further investigations, see Table 2

Table 2. Overview of all crystallographically (regular font) and spectroscopically (*in italics*) characterized non-classical polyinterhalogen anions (more than three atoms) consisting of the given halogens.^[7]

I, Br	I, Cl	I, Br, Cl	Br, Cl	Br, F
$[\text{Br}(\text{IBr})_2]^{-}$ ^[8,86]	$[\text{Cl}(\text{ICl})_2]^{-}$ ^[81–85,101]	$[\text{I}_2\text{BrCl}_2]^{-}$ ^[83]	$[\text{Br}_3\text{Cl}_5]^{2-}$ ^[102]	$[\text{F}(\text{BrF}_3)_2]^{-}$ ^[75,90–92,103]
$[\text{Br}(\text{IBr})(\text{Br}_2)]^{-}$ ^[95]	$[\text{Cl}(\text{ICl})_3]^{-}$ ^[85,104]	$[\text{I}_2\text{Br}_2\text{Cl}_4]^{2-}$ ^[99]	$[\text{Br}_4\text{Cl}_4]^{2-}$ ^[102]	$[\text{F}(\text{BrF}_3)_3]^{-}$ ^[83,92,103]
$[\text{I}_5\text{Br}_2]^{-}$ ^[85,86]	$[\text{Cl}(\text{I}_2)_4]^{-}$ ^[30]	$[\text{I}_3\text{BrCl}_4]^{2-}$ ^[99]	$[\text{Br}_{6.56}\text{Cl}_{1.44}]^{2-}$ ^[102]	
$[\text{Br}(\text{IBr})_3]^{-}$ ^[85,87,88]	$[\text{I}_{9.74}\text{Cl}_{1.26}]^{-}$ ^[96]	$[\text{I}_4\text{Br}_2\text{Cl}_2]^{2-}$ ^[99]		
$[\text{I}_4\text{Br}_5]^{-}$ ^[8]	$[\text{I}_2\text{Cl}_7]^{-}$ ^[105]	$[\text{I}_2\text{Br}_4\text{Cl}_2]^{2-}$ ^[99]		
$[\text{Br}-\text{I}-\text{I}-\text{Br}]^{2-}$ ^[94]	$[\text{Cl}-\text{I}-\text{I}-\text{Cl}]^{2-}$ ^[93,94]	$[\text{I}_3\text{Br}_3\text{Cl}_2]^{2-}$ ^[99]		
$[\text{I}_2\text{Br}_6]^{2-}$ ^[95,97]	$[\text{I}_4\text{Cl}_4]^{2-}$ ^[85,98]			
$[\text{I}_3\text{Br}_5]^{2-}$ ^[97]	$[\text{I}_{3.77}\text{Cl}_{4.23}]^{2-}$ ^[96]			
$[\text{I}_3\text{Br}_5]^{2-}$ ^[97]	$[\text{I}_3\text{Cl}_5]^{2-}$ ^[98]			
$[\text{I}_{4.24}\text{Br}_{3.76}]^{2-}$ ^[96]	$[\text{I}_{3.6}\text{Cl}_{4.4}]^{2-}$ ^[98]			
$[\text{I}_{6.67}\text{Br}_{1.33}]^{2-}$ ^[96]	$[\text{I}_6\text{Cl}_6]^{2-}$ ^[85]			
$[\text{I}_5\text{Br}_7]^{2-}$ ^[100]	$[\text{Cl}_2\text{I}_{14}]^{2-}$ ^[26]			

1.3.5 Polypseudohalogen Anions

The knowledge of polyhalogen chemistry increased significantly over the last decades and resulted in the synthesis and characterization of a variety of small and large poly(inter)halogen anions, such as $[\text{F}_5]^-$ ^[41,42], $[\text{Cl}_{13}]^-$ ^[111] and $[\text{I}_4\text{Br}_9]^-$.^[8] In contrast, the chemistry of polypseudohalogen anions is significantly less studied.

Generally, a pseudohalogen is defined by IUPAC as a polyatomic moiety that resembles the halogens X_2 or interhalogens XY in their chemistry.^[32] Symmetric pseudohalogens, such as cyanogen $(\text{CN})_2$ and thiocyanogen $(\text{SCN})_2$, are comparable to halogens such as Br_2 and Cl_2 . Non-symmetric pseudohalogens, such as iodine azide, IN_3 , or the cyanogen halides, ClCN , BrCN , and ICN , correspond to the interhalogens (e.g. IBr , BrCl). Furthermore, anions, such as azide N_3^- or cyanide CN^- , that have sufficient resemblance to halides, like Cl^- and Br^- , are referred to as pseudohalogen anions.^[32] Accordingly, it is possible to obtain polypseudohalogen anions by replacing at least one halogen atom of a polyhalogen compound with a pseudohalogen group.^[33] Since they are rather difficult-to-handle and often instable, only a few pseudohalogen anions are known. The most stable polyhalogen species is the trihalogen monoanion (e.g. $[\text{Br}_3]^-$, $[\text{Cl}_3]^-$).^[7] Thus, it is not surprising that the most frequently reported polypseudohalogen species are trihalogen monoanion analogues, such as the compounds $[(\text{SeCN})_3]^-$ ^[106] and $[(\text{NCS})\text{I}_2]^-$.^[107] Another noteworthy polypseudohalogen ion was structurally characterized in $[\text{PPh}_4][\text{I}(\text{N}_3)_2]$. The $[\text{I}(\text{N}_3)_2]^-$ anion consists of a central iodine atom which is almost linearly connected (N-I-N : 178.4°) to two end-on coordinating azides, see Figure 19.^[108]

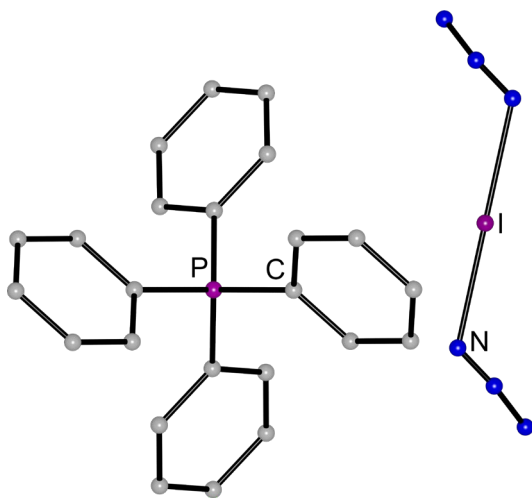


Figure 19. Molecular structure of $[\text{PPh}_4][\text{I}(\text{N}_3)_2]$ in the solid state. Ellipsoids are not shown because thermal factors were not provided by the CCDC database.^[108]

The structural flexibilities by replacing a halogen atom with a polyatomic pseudohalogen group were discussed by Tebbe and Fröhlich in the early 1980s. In the following years they reported the structural relations of polyhalogen and polypseudohalogen anions and were able to synthesize several novel polypseudohalogen compounds.^[109,110] In addition to the almost linear trihalogen monoanion analogues $[\text{I}(\text{CN})_2]^-$ ^[110,111] and $[\text{I}(\text{ICN})]^-$ ^[110], they reported the pentahalogen monoanion analogues $[\text{Br}(\text{ICN})_2]^-$ ^[110] as well as $[\text{I}(\text{ICN})_2]^-$ ^[33,110,112] for the first time. The latter consists of a central I⁻ that is coordinated by two ICN molecules in a V-shaped structure (Figure 20), similar to the pentainterhalogen monoanions, such as $[\text{Cl}(\text{ICl})_2]^-$ ^[84].

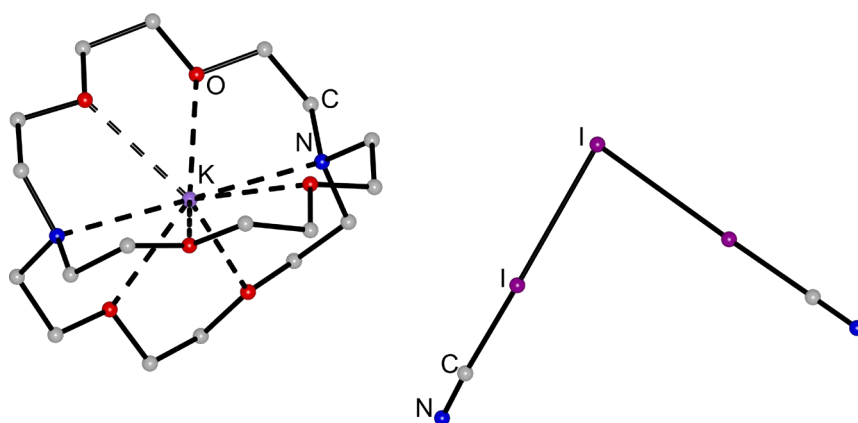


Figure 20. Molecular structure in the solid state of the polypseudohalogen monoanion $[\text{I}(\text{ICN})_2]^-$ in $[\text{K}(\text{crypt-2.2.2})][\text{I}(\text{ICN})_2]^-$. Ellipsoids are not shown because thermal factors were not provided by the CCDC database.^[33]

In 1979, Alcock and Sawyer considered $[\text{NMe}_2]^-$ as a new pseudohalogen anion and reported on the solid state structure of $[\text{NMe}_4][\text{Me}_2\text{N}(\text{ICl})_2]$.^[113] The polypseudohalogen monoanion $[\text{Me}_2\text{N}(\text{ICl})_2]^-$ is built of a $[\text{NMe}_2]^-$ unit that is connected to two ICl molecules via the nitrogen atom, which in turn is coordinated tetrahedrally, see Figure 21. This structural motif makes it comparable to known pentainterhalogen monoanions.^[113]

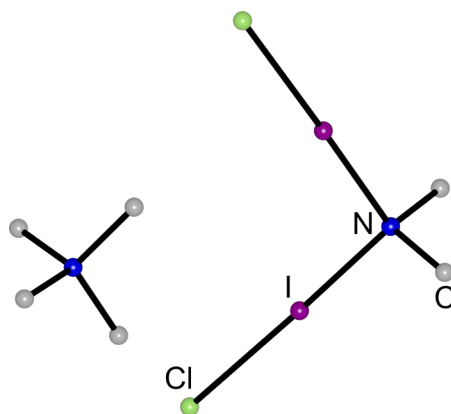


Figure 21. Solid-state structure of $[\text{NMe}_4][\text{Me}_2\text{N}(\text{ICl})_2]$. Ellipsoids are not shown because thermal factors were not provided by the CCDC database.^[113]

The concept of halogen bonding can therefore be expanded to pseudohalogens and enables the synthesis and characterization of several polypseudohalogen compounds. However, to the best of the author's knowledge, no polypseudohalogen monoanions, which resemble hepta- or higher polyinterhalogen molecules, or dianions are known to date.

1.4. Ionic Liquids

The first room temperature ionic liquid (RT-IL), ethylammonium nitrate, was already synthesized by Walden in 1914 by reacting ethylamine with concentrated nitric acid.^[114] Nowadays, the commonly accepted term for low-melting salts is ionic liquid (IL), which is defined as an ionic material with a melting point below 100 °C.^[115,116]

Classical salts, such as sodium chloride, possess high melting points above ambient temperatures. This can be explained by a dense packing of cations and anions of similar size and high symmetry, which leads to a high lattice energy in the solid due to strong attractive electrostatic interactions. In contrast, a decrease in lattice energy can be achieved by a less dense packing owing to differently sized or asymmetric ions. Consequently, low melting points are enabled by ionic liquids that, for example, are built of a bulky asymmetric cation and a simple halide. Commonly used for the synthesis of ILs are asymmetric organic cations, such as imidazolium, pyrrolidinium, pyridinium and ammonium. Typical anions of ILs include trifluoromethanesulfonate (triflate), bis(trifluoromethylsulfonyl)imide (triflimide, NTf₂), simple halides like chloride and bromide, or hexafluorophosphate, see Figure 22.^[117–120]

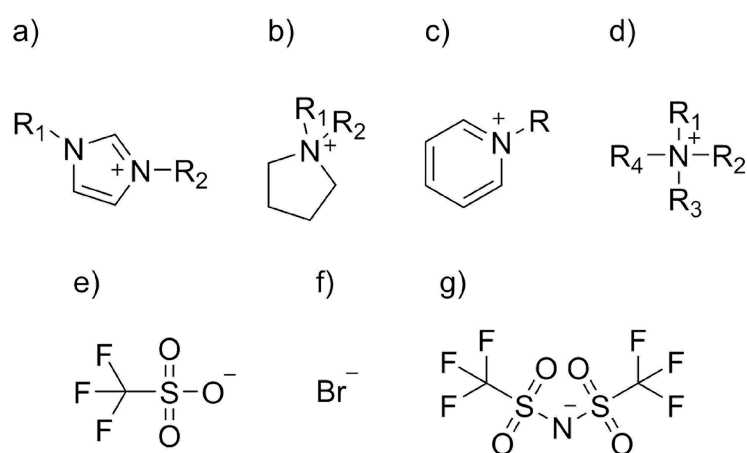


Figure 22. Selection of frequently used cations (top) and anions (bottom) in ILs: a) imidazolium, b) pyrrolidinium, c) pyridinium, d) ammonium; e) triflate, f) bromide, g) triflimide.

In general, the higher the symmetry and the charge of the ions, the higher the melting point of the IL. Since organic cations normally only have a single positive charge, the melting temperature of the IL is most influenced by the asymmetry and lengths of the substituents (mostly alkyl chains). While an initial lengthening of the alkyl chain leads to a decrease in the lattice energy and consequently the melting point, further lengthening can cause the opposite due to attractive van der Waals forces between the chains that results in a denser packing.^[115,120] Ionic liquids do not share the high melting point of usual salts like sodium chloride but have

other advantageous properties in common. This includes a very low vapor pressure and flammability as well as a high thermal stability. Additionally, most ILs possess a wide liquid-phase range, a low toxicity and offer a large electrochemical window.^[117-120] By varying the substituents of the cations or anions and by permutation of the ions themselves, it is possible to synthesize a vast number of ILs. This enables the design of desired properties that are typical of solvents, such as viscosity, thermal and chemical stability as well as polarity.^[9] Furthermore, the introduction of selected functional groups or metals into the IL offers specific physicochemical properties, such as catalytic activity^[120,121], luminescence^[122,123] or magnetism^[124]. Because of their unique features and the opportunity for countless modifications by tailoring cation and anion, ILs have been referred to as “designer solvents” and “green solvents”.^[125] These advantages of a new class of solvents offer new perspectives for inorganic synthesis, which has been reported by Feldmann and co-workers.^[9] Due to the use of ILs as solvents, it was possible to stabilize low-valent rare earth metal cations, such as Eu^{2+} , in the IL 1-butyl-3-methylimidazolium hexafluorophosphate. Besides the observed luminescence caused by Eu^{2+} , it was shown, that the IL prevents the oxidation of Eu^{2+} to Eu^{3+} despite the presence of light or addition of oxidizing agents like $\text{K}_2\text{Cr}_2\text{O}_7$ or $\text{Ce}(\text{SO}_4)_2$.^[123] The combination of thermal stability and polarity as well as the good solubility of elemental metals in the IL enables reducing conditions and access to compounds with metal-metal bonds and clusters.^[9] Apart from their great stability against strong reducing agents, e.g. potassium, some ILs are stable against strong oxidizers. For example, it has been shown that ILs are not only stable against halogens, such as Br_2 and Cl_2 , but are also able to dissolve a large amount of halogen and drastically reduce its vapor pressure. This enabled the synthesis and characterization of large polyhalogen anions, such as $[\text{Br}_{20}]^{2-}$ ^[69] (section 1.3.3) and $[\text{Cl}_8]^{2-}$ ^[10] (section 1.3.2). Interestingly, the preparation of these polyhalogen compounds led to the access to novel ionic liquids, which in turn possess unique properties, such as unusually high conductivities.^[126] These poly(inter)halogen anion based ILs offer a variety of application possibilities (see section 1.5), whose researches have only just begun.

1.5. Applications of Ionic Liquids Based on Polyhalogen Anions

The knowledge of halogen bonding and the diversity of structural motifs of polyhalogen and polyinterhalogen anions increased steadily over the last years. The resulting expertise also led to an increased interest in possible applications that could be achieved through the synthesis of ionic liquids based on these manifold species. Currently, the use of poly(inter)halogen compounds can be divided into three main areas of application: firstly, in the field of electrochemistry due to the high conductivity of the polyhalogen species, secondly, their use as halogenation reagents in organic and inorganic syntheses, and thirdly, as reactive material in metal recycling.^[7]

1.5.1 Electrochemical Applications

Electrochemical investigations of polyhalogen compounds revealed surprisingly high conductivities. For instance, the RT-IL [HMIM][Br₉] (HMIM = 1-hexyl-3-methylimidazolium) shows a conductivity of 52.1 mS cm⁻¹ at 25 °C (Figure 23), which is a thousand times higher than neat [HMIM]Br (54.1 μS cm⁻¹).^[126] Usually, the conductivities of ILs based on imidazolium cations are in the range of 1 – 10 mS cm⁻¹ at 25 °C.^[126,127] However, the unorthodox high conductivities of ILs based on polyhalogen anions can be explained by a Grotthus-type hopping mechanism comparable to that of water.^[126,128]

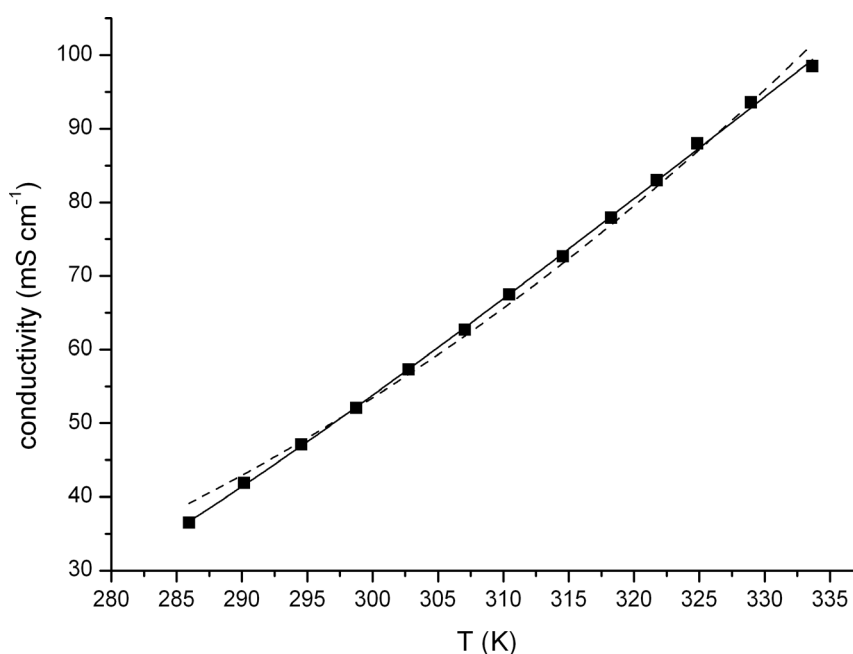


Figure 23. Temperature dependent conductivity of [HMIM][Br₉], analyzed with respect to Arrhenius (dashed line) and Vogel-Fulcher-Tammann (continuous line).^[126]

Dye-sensitized solar cells possess the potential for low-cost solar energy conversion, which explains the ongoing research on this topic. The photoelectrochemical system of these cells consists of a monolayer of sensitizing dye that is adsorbed onto a TiO₂ electrode. The gap between both electrodes is filled by a redox couple containing electrolyte. Nowadays, the most prominent redox mediator is the I⁻/[I₃]⁻ system because of its good solubility, suitable redox potential, and rapid dye regeneration. In addition, the redox couple shows very slow recombination kinetics between electrons in TiO₂ and [I₃]⁻.^[129] The analogous redox mediator Br⁻/[Br₃]⁻ has an even higher open circuit photopotential and a higher overall conversion efficiency, nevertheless, the corrosive properties of elemental bromine are still a challenging problem that needs to be considered.^[130] Furthermore, polyhalogen anions can be used in redox flow batteries, e.g. the zinc-bromine battery. Elemental Br₂ is an excellent electro active species with fast and reversible kinetics. However, the high vapor pressure of the toxic Br₂ requires complexing agents within the battery that do not interfere with the electrochemical properties. The addition of bromide salts, such as 1-ethyl-1-methylpyrrolidinium bromide, immediately leads to the formation of ILs based on polybromine anions, which consequently reduce the vapor pressure and inhibit the corrosion, toxicity, and self-discharge of Br₂ by forming an immiscible emulsion in the close proximity to the electrodes.^[131,132] These polybromine species containing emulsions act beyond their function as complexing agents and further contribute as reactants in the electrochemistry of Br⁻.^[132,133] Recently, investigations on current amplifications of single microdroplets of a Br⁻/[Br_{2n+1}]⁻-based IL were performed. It was shown that the charge transport is even faster by one magnitude than the Grotthuss-like hopping mechanism of protons.^[134]

1.5.2 Halogenation Reactions

The halogenation of certain molecules, e.g. alkenes, alkynes, and Michael systems, is an important reaction in organic syntheses. However, the use of the partially gaseous and highly toxic halogens requires strict safety precautions. To avoid the handling of elemental halogens, polyhalogen anions represent a safer alternative as halogenation reagents. Trihalogen monoanions such as $[\text{Br}_3]^-$ exist as stable, solid bulk materials or RT-ILs with extremely low vapor pressures.^[135] In the reaction mechanism of an alkene bromination, the Br_2 molecule is polarized by the π -electrons of the double bond causing a partial positive charge of the bromine atom closer to the bond. An attack of the double bond leads to a heterolytic cleavage of the $\text{Br}-\text{Br}$ bond and the formation of the intermediate bromonium ion (three-membered ring), which is subsequently attacked at the backside by the remaining Br^- , yielding an *anti*-addition product, see Figure 24.^[136]

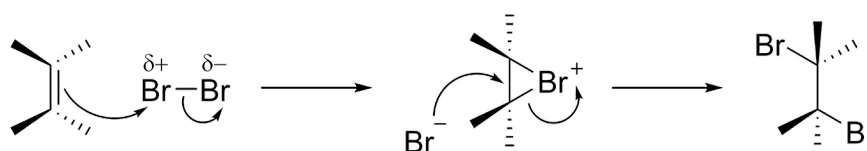


Figure 24. Reaction mechanism of the bromine addition to an alkene.^[125]

Investigations of bromination reactions with tri- and nonabromine compounds showed even higher efficiencies and regioselectivities than reactions with elemental bromine.^[137,138] This may be explained by pre-polarization of the $\text{Br}-\text{Br}$ bond in polybromine species, which results in bond weakening and thus to a simplified first step of the reaction mechanism.^[138] A similar reaction behavior is reported for trichlorine monoanions, which act as an easy-to-handle alternative to gaseous Cl_2 in chlorination reactions. The investigations revealed possible chlorinations of various substrates such as alkenes^[139], alkynes^[140,141] or ketones^[140] and thus enable the usage of $[\text{Cl}_3]^-$ in areas such as total synthesis.^[142]

In contrast to the described dihalogenation with homonuclear halogens like Cl_2 or Br_2 , the regio- and stereoselective addition of two different halogens (heterodihalogenation or interhalogenation) to an alkene is more challenging. Recently, Teichert discussed the ongoing problems of the interhalogenation reaction and its importance for the synthesis of natural products.^[143,144] Furthermore, the current research on synthetic methods of interhalogenated natural products, such as the cytotoxic antitumor agent halomon, which was originally isolated from red algae, was highlighted.^[143,145,146] Nevertheless, preclinical studies of halomon had to be canceled, because insufficient amounts could be provided.^[146]

Consequently, further research on interhalogenation agents is highly desired. A promising approach is the use of polyinterhalogen compounds based on interhalogens, such as IBr or BrCl. Because of the even more pre-polarized bond of the interhalogen molecules in the polyinterhalogen species (see section 1.2., Figure 4), the heterodihalogenation might be simplified. After initial investigations of $[\text{NBu}_4][\text{Cl}(\text{BrCl})]$ showed promising results in the 1980s^[147], the total synthesis of halomon was carried out with this reagent in 2000.^[148] However, further investigations are required to stabilize, for example, the gaseous and toxic BrCl in the form of polyinterhalogen based ILs and to characterize these compounds in terms of their possible applications in interhalogenation reactions.

1.5.3 Reactive Ionic Liquids for Metal Recycling

In the last years, publications on the use of polyhalogen compounds as reactive ionic liquids have increased. In addition to their advantages as RT-ILs with low viscosities and vapor pressures, they possess strong oxidizing properties that can be used to dissolve noble metals and alloys.^[149–152]

First investigations concerning the oxidative dissolution of metals and alloys with ILs based on trichlorine anions were reported by Binnemans and co-workers in 2018.^[149] They synthesized a series of RT-ILs by varying the cation and characterized their physicochemical properties. Afterwards, a total of twelve metals (Fe, Cu, In, Zn, Ga, Sb, Au, Pt, Ge, Ta, Sm, Dy) and two alloys (GaAs, InAs) were chosen for dissolution experiments. It was shown that the complete oxidative dissolutions into the corresponding metal chlorides of both, alloys and all metals, except Pt, Ta, Sm and Dy, were successful, see Figure 25.



Figure 25. Mixtures of the ILs and the metal chlorides after complete dissolution of the corresponding metals or alloys.^[149] Reproduced from Ref. [149] with permission from the Royal Society of Chemistry.

Further research concerning the oxidative dissolution of metals was performed by changing the reactive IL. Within the studies, several ILs based on triinterhalogen monoanions consisting of different combinations of the halogens Cl, Br, and I, e.g. $[\text{BrCl}_2]^-$, $[\text{ClBr}_2]^-$ and $[\text{IBr}_2]^-$, were prepared.^[150,151] It was shown, that all RT-ILs were able to dissolve most of the metals, however, this observation is no guarantee in regards to the oxidation properties, considering the different redox potentials of the halogens.^[150] In 2018, Binnemans reported the recycling of spent samarium-cobalt magnets by $[\text{Cl}_3]^-$ containing ILs, which is crucial due to the limited resources of the metals.^[152] The reactive IL, which consists of $[\text{P}_{666,14}][\text{Cl}_3]$ ($[\text{P}_{666,14}]^+$ = trihexyltetradecylphosphonium) and an additional chloride source ($[\text{P}_{666,14}]\text{Cl}$), enabled the dissolution of SmCo powders. As depicted in Figure 26, the stripping of all metals from the loaded IL was possible in four steps, by adding a NaCl solution, water, and an NH_3 solution successively to the IL.^[152]

Furthermore, the IL could be regenerated and showed similar performances in following recycling cycles, Figure 26.^[152]

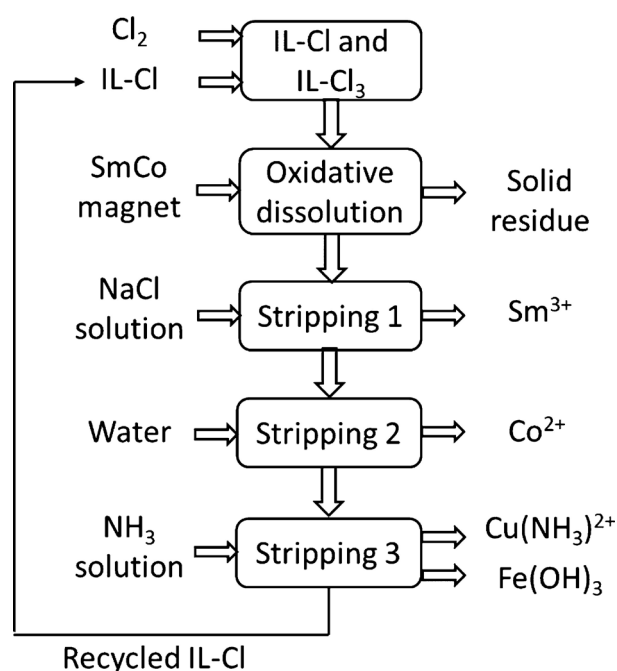


Figure 26. Scheme of the process for metal recovery of spent SmCo magnets using RT-ILs based on [Cl₃].^[151] Reproduced with permission from: <https://pubs.acs.org/doi/10.1021/acssuschemeng.8b05604>; for further permissions contact the ACS.

It was shown that ILs based on triinterhalogen anions can selectively dissolve some metals while leaving other metals untouched. Furthermore, the IL with the best properties can be selected and tailored for each specific application. Hence, the separation of mixtures of metals is possible under mild conditions and enables the application of reactive ILs as safe reagents for metal recycling, urban mining, or metal recovery from end-of-life products, such as magnets and metal hydride batteries.^[149–152]

However, further research on other ILs and their oxidative properties are required to enable the specific dissolution of the desired metals. Since aqueous etching processes of gold based on cyanide are already well established^[153], a future approach could be in the use of ILs based on pseudohalogens that contain CN⁻, such as BrCN. In addition to the described use for metal dissolving, there would also be several applications in organic chemistry. The pseudohalogen BrCN is used, for example, as a reagent for protein immobilization and in the “von Braun reaction” for the synthesis of organocyanamides from tertiary amines.^[154] Nevertheless, neat BrCN possesses a high toxicity and a relatively high vapor pressure at ambient conditions (160 mbar)^[155]. Therefore, it is desirable to combine the properties of BrCN with the advantages of ILs, such as easier handling and the significantly reduced vapor pressure.

1.6. References

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2. Objective

Since the first investigations of the triiodine monoanion in 1819, which marked the starting point of polyhalogen chemistry, numerous polyhalogen and polyinterhalogen compounds have been studied over the last two centuries. Due to its polarized bond, the interhalogen BrCl possesses a more pronounced σ -hole on the more electropositive bromine side of the molecule and is expected to form stable polyinterhalogen anions. Considering these excellent halogen bonding properties, it is surprising that no larger polyinterhalogen anions beyond $[\text{Cl}(\text{BrCl})]^-$ have been reported. One of the reasons for this is the equilibrium of BrCl with Cl_2 and Br_2 , which makes the stoichiometric use of BrCl without side products nearly impossible. Hence, a novel synthetic route that allows the stabilization of BrCl is highly desired. This might enable the synthesis of hitherto unknown polyinterhalogen compounds, which would not only contribute to the structural diversity but also could be utilized as easy-to-handle ILs for further applications. The concept of halogen bonding can be extended to pseudohalogens which are chemically similar to halogens. For example, the non-symmetric pseudohalogen BrCN can be regarded as an analogue to BrCl due to the similarly polarized bonding situation within the molecule. However, polypseudohalogen chemistry is far less researched. It is therefore desirable to synthesize polypseudohalogen species based on BrCN and to investigate their properties in terms of chemical behavior as well as potential applications in detail.

3. Publications

3.1. Synthesis and Characterization of Nonclassical Interhalides Based on Bromine Monochloride

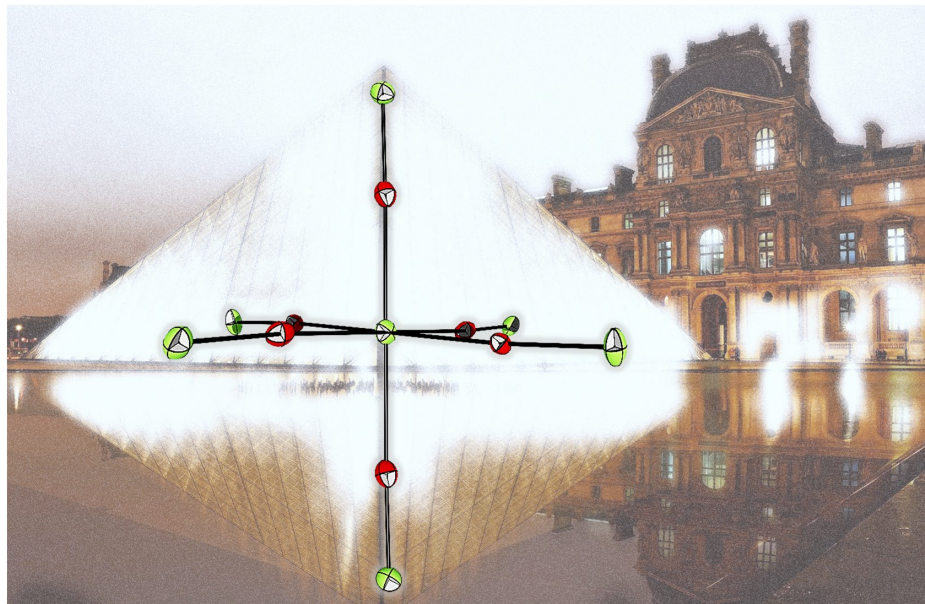


Figure 27. Table of contents graphic of the following publication presented in section 3.1.^[156]
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Benjamin Schmidt, Karsten Sonnenberg, Helmut Beckers, Simon Steinhauer, and Sebastian Riedel*

Angewandte Chemie International Edition **2018**, 57, 9141; *Angewandte Chemie* **2018**, 130, 9279.

<https://doi.org/10.1002/anie.201803705>

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Author contributions

Benjamin Schmidt designed the project and performed the experiments, quantum-chemical calculations, and product characterizations. Additionally, he wrote the publication. Karsten Sonnenberg performed the XRD measurements. Simon Steinhauer, Helmut Beckers and Sebastian Riedel managed the project, provided scientific guidance, and corrected the manuscript.

Pages 47-66 contain the printed article and were removed for copyright reasons.

The article including Supporting Information is available at

<https://doi.org/10.1002/anie.201803705>

3.2. From Polyhalides to Polypseudohalides: Chemistry Based on Cyanogen Bromide



Figure 28. Table of contents graphic of the following publication presented in section 3.2.^[24]
© Wiley-VCH Verlag GmbH & Co. KGaA

Benjamin Schmidt, Benjamin Schröder, Karsten Sonnenberg, Simon Steinhauer, and Sebastian Riedel*

Angewandte Chemie International Edition **2019**, *58*, 10340; *Angewandte Chemie* **2019**, *131*, 10448.

<https://doi.org/10.1002/anie.201903539>

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Author contributions

Benjamin Schmidt designed the project and performed most of the experiments, quantum-chemical calculations, and product characterizations. Additionally, he wrote the publication. Benjamin Schröder did some initial work during his master's thesis. Karsten Sonnenberg performed the XRD measurements. Simon Steinhauer and Sebastian Riedel managed the project, provided scientific guidance, and corrected the manuscript.

Pages 68-109 contain the printed article and were removed for copyright reasons.

The article including Supporting Information is available at

<https://doi.org/10.1002/anie.201903539>

3.3. *In Situ* Synthesis and Applications for Polyinterhalides Based on BrCl

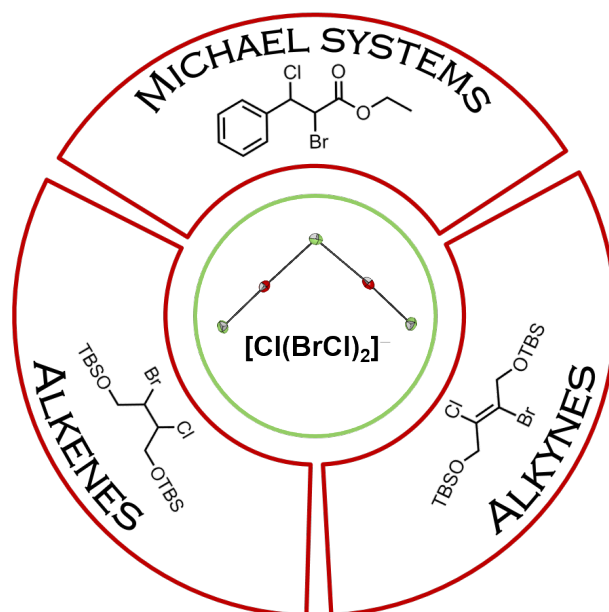


Figure 29. Table of contents graphic of the following publication presented in section 3.3.^[17]
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Benjamin Schmidt, Sebastian Ponath, Johannes Hannemann, Patrick Voßnacker, Karsten Sonnenberg, Mathias Christmann, and Sebastian Riedel*

Chemistry – A European Journal **2020**, accepted author manuscript.

<https://doi.org/10.1002/chem.202001267>

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Author contributions

Benjamin Schmidt designed the project and performed most of the experiments, quantum-chemical calculations, and product characterizations. Additionally, he wrote the publication. Sebastian Ponath performed the interhalogenation reactions and their characterizations. Johannes Hannemann performed some first work during his bachelor's thesis under guidance of Benjamin Schmidt. Karsten Sonnenberg and Patrick Voßnacker performed the XRD measurements. Mathias Christmann and Sebastian Riedel managed the project, provided scientific guidance, and corrected the manuscript.

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<https://doi.org/10.1002/chem.202001267>

4. Summary

Polyhalogen compounds and their potential applications have been investigated over a period of more than 200 years. In comparison to symmetric halogens such as Cl_2 and Br_2 , interhalogens, like BrCl , or pseudohalogens, such as BrCN , possess a highly polarized bond. Quantum-chemical calculations of the electrostatic potentials showed that BrCl and BrCN have pronounced σ -holes at the bromine side of the molecules, which induces strong halogen bonds and favors the formation of stable and more discrete anions rather than extensive polyhalogen networks.

Remarkably, no larger BrCl based polyinterhalogen anions than $[\text{Cl}(\text{BrCl})]^-$ were known in the literature. This might be explained by the hindered access to pure BrCl , due to its equilibrium with Br_2 and Cl_2 , as well as its severe toxicity and gaseous state of matter. In the present work, the synthesis and characterization of a complete set of possible polyinterhalogen monoanions $[\text{Cl}(\text{BrCl})_n]^-$ ($n = 2 - 6$) with two to six coordinating BrCl molecules was presented.

This was enabled by the use of bulky or highly symmetric cations, respectively. All novel polyinterhalogen monoanions can be described as donor-acceptor complexes and consist of a central chloride that functions as a Lewis base and a varying number of surrounding BrCl molecules, the Lewis acids. The set of new polyinterhalogen compounds contains the V-shaped $[\text{Cl}(\text{BrCl})_2]^-$, the trigonal-pyramidal $[\text{Cl}(\text{BrCl})_3]^-$, the distorted tetrahedral $[\text{Cl}(\text{BrCl})_4]^-$ as well as the five times coordinated $[\text{Cl}(\text{BrCl})_5]^-$, whose structure can be described as rather square-pyramidal than trigonal-bipyramidal as indicated by the structural parameter τ . On top of that, the first and hitherto only tridecainterhalogen monoanion was stabilized by the weakly coordinating cation $[\text{PNP}]^+$. The reported octahedral structural motif of $[\text{Cl}(\text{BrCl})_6]^-$ is very rare in polyhalogen chemistry and defines the largest non-classical polyinterhalogen monoanion to date. All BrCl based compounds were thoroughly characterized by X-ray diffraction, Raman spectroscopy as well as high-level quantum-chemical calculations.

In addition to the expansion of the structural diversity of polyhalogen anions, a new *in situ* synthesis route is presented for polyinterhalogen compounds based on BrCl . In this approach, a chloride salt is provided and the interhalogen BrCl is generated *in situ* after elemental Cl_2 and Br_2 were stoichiometrically condensed onto the salt. The nascent BrCl immediately reacts with the Cl^- to afford the desired polyinterhalogen species. Addition of the Lewis base Cl^- shifts the equilibrium significantly to the BrCl side (>99.99 %). For larger $[\text{Cl}(\text{BrCl})_n]^-$ anions, quantum-chemical calculations indicate relatively weak bonding between the central Cl^- and

the coordinating BrCl molecules. Consequently, those polyinterhalogen compounds can function as direct source of pure BrCl, minimizing impurities of Cl₂ and Br₂. This enables the use of BrCl as a valuable reagent, as shown by the synthesis of reactive ILs and their use in heterodihalogenation reactions. The preparation of these ILs, which are easy-to-handle and have very low vapor pressures, was achieved by the use of asymmetric cations, such as [NEt₃Me]⁺. Concerning their reactivity, interhalogenation studies with alkenes, alkynes and Michael systems, were performed, resulting in very short reaction times and good yields even at low temperatures.

By transferring the experience of the tunable influences on the structural diversity and properties in polyhalogen chemistry, a new class of polypseudohalogen compounds based on BrCN was reported. BrCN possesses an even more pronounced σ -hole than BrCl. It was possible to isolate the polypseudohalogen salts [PNP][Br(BrCN)] and [PNP][Br(BrCN)₃]. Similar to the polyinterhalogen monoanions, the new compounds consist of a central halide that is coordinated by either one BrCN molecule in an almost linear structure or by three BrCN molecules in a distorted trigonal-pyramidal structure. Both compounds were characterized by XRD, Raman spectroscopy as well as quantum-chemical calculations. Moreover, ¹³C and ¹⁵N NMR spectra of diluted and neat samples of the polypseudohalogen ILs were recorded, indicating a fast equilibrium between different [Br(BrCN)_n]⁻ species at ambient conditions. Once more, the use of asymmetric cations led to the formation of RT-ILs, which possess a vapor pressure reduced by at least a factor of ten compared to neat BrCN. Hence, the risk of exposition to toxic BrCN is minimized. Additionally, these reactive ILs are capable of dissolving elemental gold because of their oxidative properties.

All in all, a new *in situ* synthesis route for polyinterhalogen compounds was developed and enables the access to a source of pure BrCl, which can subsequently be used for the challenging heterodihalogenation in the synthesis of natural products. Furthermore, the use of bulky, symmetric cations allowed the isolation of hitherto unknown molecular structures in the solid-state containing [Cl(BrCl)_n]⁻ ($n = 2 - 6$) as well as [Br(BrCN)_n]⁻ ($n = 1, 3$). On the contrary, asymmetric cations led to the formation of reactive RT-ILs. The present work shows promising perspectives for the application of these versatile compounds. Due to the different oxidation strengths, selective metal recycling and recovery as well as urban mining are possible key features of the various polyinterhalogen and polypseudohalogen anions in the future.

5. Publications and Conference Contributions

5.1. Publications

- (1) **B. Schmidt**, K. Sonnenberg, H. Beckers, S. Steinhauer, S. Riedel, *Angew. Chem. Int. Ed.* **2018**, *57*, 9141; *Angew. Chem.* **2018**, *130*, 9279.
<https://doi.org/10.1002/anie.201803705>
- (2) **B. Schmidt**, B. Schröder, K. Sonnenberg, S. Steinhauer, S. Riedel, *Angew. Chem. Int. Ed.* **2019**, *58*, 10340; *Angew. Chem.* **2019**, *131*, 10448.
<https://doi.org/10.1002/anie.201903539>
- (3) K. Sonnenberg, L. Mann, F. A. Redeker, **B. Schmidt**, S. Riedel, *Angew. Chem. Int. Ed.* **2020**, *59*, 5464; *Angew. Chem.* **2020**, *132*, 5506.
<https://doi.org/10.1002/anie.201903197>
- (4) **B. Schmidt**, S. Ponath, J. Hannemann, P. Voßnacker, K. Sonnenberg, M. Christmann, S. Riedel, *Chem. Eur. J.* **2020**, accepted author manuscript.
<https://doi.org/10.1002/chem.202001267>

5.2. Conference Contributions – Oral Presentations

- (1) **B. Schmidt**, S. Riedel: Synthesis and Applications of Novel Polyhalides, *253rd American Chemical Society National Meeting & Exposition*, San Francisco, USA, **2017**.
- (2) **B. Schmidt**, S. Riedel: From Polyhalides to Polypseudohalides – Chemistry with BrCl and BrCN, *7. Tag der Anorganischen Chemie*, Freie Universität Berlin, Germany, **2019**.

5.3. Conference Contribution – Poster Presentations

- (1) **B. Schmidt**, K. Sonnenberg, S. Riedel: Non-classical Interhalides Based on Bromine Monochloride, *5. Tag der Anorganischen Chemie*, Freie Universität Berlin, Germany, **2017**.
- (2) **B. Schmidt**, K. Sonnenberg, S. Riedel: Synthesis and Characterization of Nonclassical Interhalides Based on Bromine Monochloride, *6. Tag der Anorganischen Chemie*, Freie Universität Berlin, Germany, **2018**.
- (3) **B. Schmidt**, S. Riedel: Synthesis and Characterization of Nonclassical Interhalides Based on Bromine Monochloride, *19. Vortragstagung der Wöhler-Vereinigung*, Regensburg, Germany, **2018**.

6. Curriculum Vitae

The curriculum vitae is not included for reasons of data protection.