Polyinterhalides

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Iodine–Iodine Bonding makes Tetra(diiodine)chloride, $[Cl(I_2)_4]^-$, Planar**

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Dedicated to Professor Werner Uhl on the occasion of his 60th birthday

When halide ions and halogen molecules are combined in an appropriate solvent they assemble to higher aggregates. With the right choice of cation, it is possible to crystallize polyhalide anions as salts. The most stable polyhalide ion is the triiodide ion, $[I_3]^-$, now known for almost two centuries, although a first crystal structure, that of $(NH_4)[I_3]$, was only determined in 1935.[1] The $[I_3]^-$ ion may be understood as an addition of iodine to iodide. Triiodide anions, as known from hundreds of salts, are often non-symmetric which supports the idea of a donor–acceptor/acid–base species produced from I^- and I_2. Nevertheless there are also many symmetric, linear triiodides, $[I_3]^-$ as shown by Raman spectroscopy. Thus, the triiodide anion is certainly a species in its own right. Higher polyiodides, with up to 29 iodine atoms and charges of up to −3, are less abundant, especially as isolated species.[2,3] Polybromide and polychloride species have been observed, although in far less abundance. The trifluoride anion, $[F_3]^-$, has to date only been observed in solid noble-gas matrices.[4]

Polyinterhalides are well established, such as the classic linear $[ICl_2]^-$ or tetrahedral $[ICl_4]^-$ ions.[5,6] Little is known about the chemical bonding in such compounds. Typically the central halogen atom is ascribed a positive oxidation state and the complex ion is described again as a donor–acceptor/acid–base species. Adducts of an electronegative central anion, such as Cl^-, with halogen molecules, such as I_2, attached, are not known. We have now, in our attempts to form polyiodide networks around large cations, built of metal cations encapsulated in crown ethers, observed the anion with a formula of $[ClI_8]^-$ which can be described as $[Cl(I_2)_4]^-$.

We first observed the formation of $[Cl(I_2)_4]^-$ when treating YI_3 with benzo-15-crown-5 (b15c5), sodium chloride, and iodine in methanol (with a few drops of hydroiodic acid) which yielded dark red to black plates of $[(H_5O_2)(I_2b15c5)_2][Cl(I_2)_4]$ (**1**; for details of the crystal structure determination of **1** see the Supporting Information) and yellow needles or plates of $[(H_5O_2)(I_2b15c5)_2][ICl_2](I_2b15c5)_2$ (**2**). A more straightforward synthesis of **1** is by the reaction of ICl, iodine, and b15c5 in methanol. In both reactions, with YI_3 and with ICl, two hydrogen atoms in the 3 and 4 positions of the benzo ring are substituted by iodine atoms in a Friedel–Crafts reaction. Two of these I_2b15c5 molecules with opposite orientations include a $(H_5O_2)^+$ ion, yielding the cation as shown in Figure 1. The O–O distance in the O···H··O bridge is at 244(1) pm the same as in $(H_5O_2)(b15c5)_2[AuCl_4]$,[7] 242.0(6) pm. There are two short O–O distances of 266 pm to crown-ether oxygen atoms. Those to the remaining three oxygen atoms of I_2b15c5 are between 292 and 308 pm. In **1**, the $[(H_5O_2)(I_2b15c5)_2]^+$ ions are arranged in the (001) plane in a way that allows the diiodobenzo part of the crown ether to form van der Waals bonds which leads to the formation of cationic sheets. These cationic sheets alternate with anionic planes in the [001] direction, see Figure 2. The anionic planes are flat and contain $[Cl(I_2)_4]^-$ ions, in an arrangement that is shown in Figure 3.

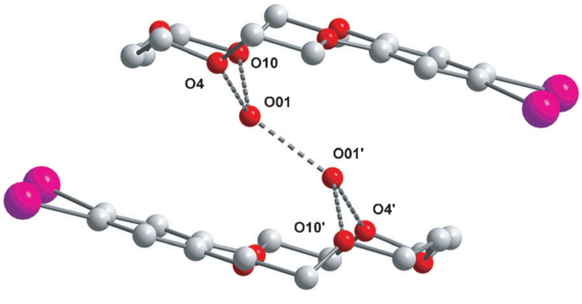

Figure 1. The cation $[(H_5O_2)(I_2b15c5)_2]^+$ as found in the crystal structures of **1** and **2**, C gray, I purple.

The most striking feature of the crystal structure of $[(H_5O_2)(I_2b15c5)_2][Cl(I_2)_4]$ (**1**) is the unprecedented anion of

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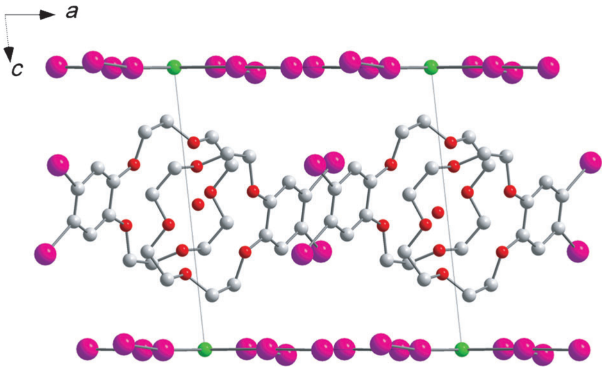

Figure 2. Crystal structure of **1** viewed down [010]. C gray, I purple, O red, Cl green.

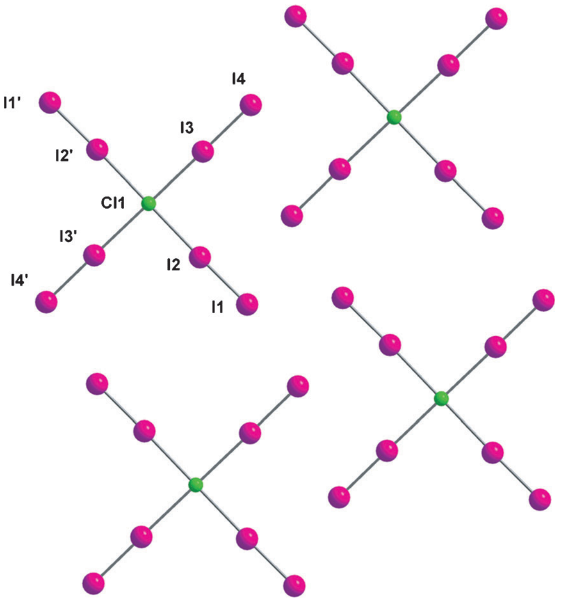

Figure 3. Part of the anionic layer of $[Cl(I_2)_4]^-$ ions in the crystal structure of **1** projected onto (001).

the $[Cl(I_2)_4]^-$ type, that is square-planar, rather than tetrahedral! The central chlorine atom can be considered as a chloride ion to which four iodine molecules with Cl$^-$-I distances of 299.6(1) and 302.9(1) pm (two times each) are attached in a square-planar configuration. The average Cl$^-$–I distance of 301 pm is considerably shorter than the sum of the ionic radius of Cl$^-$ and the covalent radius of I, 313 pm. It is, clearly and understandably, much longer than the I$^+$–Cl$^-$ (260 pm) and I^{3+}–Cl$^-$ distances (249 pm) in $[ICl_2]^-$ and $[ICl_4]^-$, respectively.[5,6]

The I-Cl-I angles in $[Cl(I_2)_4]^-$ are all 90°, within the error limits. I–I distances in the attached I_2 molecules are 269.9(1) and 270.5(2) pm, thus, are very close to the I–I distance in solid iodine at 170 K, 271.5(6) pm,[8,9] and in the inclusion compound (I_2)@(db24c8) (db24c8 = dibenzo-24-crown-8), , 268.39(7) pm.[10] I–I distances to neighboring $[Cl(I_2)_4]^-$ ions in the layer as shown in Figure 3 are between 386.7(2) and 399.7(2) pm and, therefore, fall at the limit of twice the van der Waals radius of iodine, 396 pm.[11]

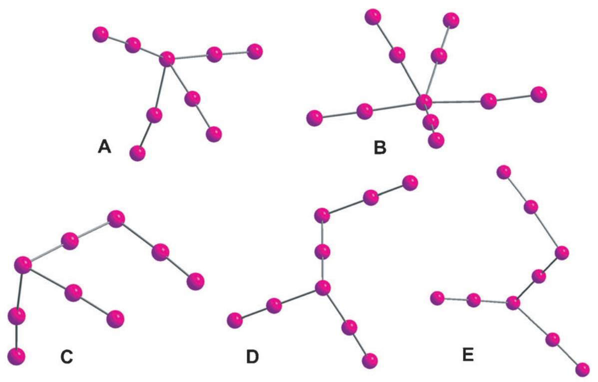

Figure 4. Structures of nona-iodide anions from single-crystal X-ray diffraction analyses. See text for references.

Although $[Cl(I_2)_4]^-$ is the only nona-interhalide to date, there are nona-halides. A small number of nona-iodides has been structurally established, of which only the structures A and B in Figure 4 come close to a $[I(I_2)_4]^-$ configuration.[12] The remaining three should rather be formulated as $[(I_3)(I_2)_3]^-$ (C, D) and $[(I_5)(I_2)_2]^-$ (E), respectively.[13–15] In A and B the mean I$^-$–I distances are, at 323 and 338 pm, much shorter than the sum of the ionic radius of iodide and the covalent radius of iodine, 353 pm. I-I-I angles in A and B range from 178.8(1) (I1-I2-I3) to 74.9(1)° (I6-I1-I4) (A) and 178.8(2) (I1-I2-I3) to 77.1(1)° (I2-I1-I6) (B), hence are considerably different from a tetrahedral structure which would demand 109.47°. Generally the same picture is seen in the nona-bromide anion, $[Br_9]^-$, which has recently been established in $[N(C_3H_7)_4][Br_9]$.[16] It must be described as $[Br(Br_2)_4]^-$ with Br$^-$–Br distances of 294.3 pm and Br–Br distances in the attached Br_2 molecules of 235 pm, slightly longer than in elemental bromine, 228 pm. The tetrahedron, however, is flattened with Br-Br-Br angles of 99.8 and 131.2°, respectively.

In all homo-nona-halides $[X(X_2)_4]^-$ with X = Br, I, the countercations are large and close to spherical shape, that is, the tetrahedral tetraethyl- or tetrapropylammonium. In $[(H_5O_2)(I_2b15c5)_2][Cl(I_2)_4]$ (**1**), the cations are far from spherical and it seems that specific cation–cation van der Waals interactions lead to the formation of cationic sheets. As a consequence, the anions also assemble in a layer, as has been described above, see Figures 2 and 3.

To tackle the questions whether it is the crystal packing that forces the tetra(diiodine)chloride, $[Cl(I_2)_4]^-$, to be planar and not tetrahedral or flattened tetrahedral as in the only $[Br_9]^-$ ion and the few $[I_9]^-$ ions, quantum-chemical calculations have been carried out. The ground-state structure and electronic structure of $[Cl(I_2)_4]^-$ was investigated with density functional theory (DFT), second order Møller-Plesset perturbation theory (MP2), and spin-scaled MP2 (SCS-MP2). For DFT the BP86 functional was used. For structure optimizations of the monomers the doubled polarized triple-ζ-basis set def2-TZVPP was used within the framework of the *r*esolutions-of-the-identity approximation. Structure optimization on all levels of theory leads to the tetrahedral structure of the anion with roughly similar bonding angles and interatomic distances (Figure 5, left).

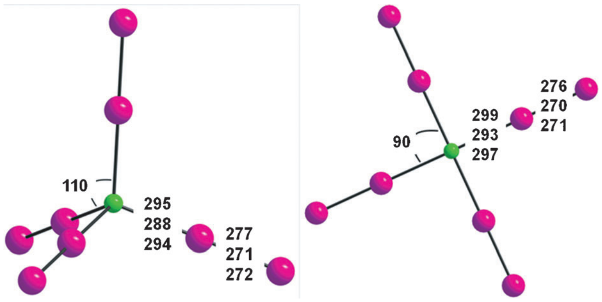

Figure 5. Calculated ground state structure (left) and square-planar structure (right) of $[Cl(I_2)_4]^-$: Distances (in pm) calculated with RI-BP86/def2-TZVPP, fc-RI-MP2/def2-TZVPP, and fc-RI-SCS-MP2/def2-TZVPP (top to bottom).

Calculations on the square-planar $[Cl(I_2)_4]^-$ ion as it exists in the crystal, reveals that the square-planar structure is a transition state in the gas phase. This situation was found by frequency analysis, where exactly one imaginary mode was obtained, classifying this structure as a saddle point on the potential hypersurface. As the computed imaginary frequency is below 10 cm^{-1} at all levels used it can be expected that the potential hypersurface is very shallow. The structure of the calculated transition state is shown in Figure 5 (right).

On the basis of DFT calculations, the square-planar transition-state configuration is about 21 $kJ\,mol^{-1}$ higher in energy than the tetrahedral ground state. Calculations at MP2 and SCS-MP2 level of theory show an energy difference of only 6 and 8 $kJ\,mol^{-1}$, respectively. These values are in the typical range of weak interactions. It should therefore be possible to overrule this small energy difference through packing effects in crystalline $[(H_5O_2)(I_2b15c5)_2][Cl(I_2)_4]$. To further elucidate this assumption the electrostatic potential for both configurations was computed at the RI-BP86/def2-TZVPP level of theory. Figure 6 shows plots of the electrostatic potential for the electron density with an isovalue of 0.01 for both tetrahedral and planar geometry.

These calculations clearly show that the crystal packing as observed in the experiment (Figure 3) can be explained by the interaction of $[Cl(I_2)_4]^-$ units with each other. The peripheral region of the I_2 molecule of $[Cl(I_2)_4]^-$ has a higher potential than the lateral side, the so-called σ-holes.[17,18] When the peripheral regions interact with the lateral sites, additional energy is gained.

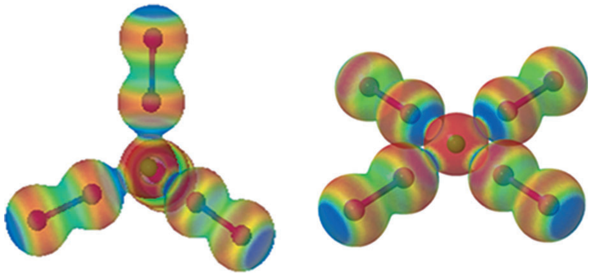

Figure 6. Electrostatic potential for the tetrahedral and square-planar geometry of $[Cl(I_2)_4]^-$ computed at the RI-BP86/def2-TZVPP level of theory.

This interaction is shown by the investigation of the potential energy surface at SCS-MP2/def2-TZVPP level for the dimeric structure $[\{Cl(I_2)_4\}_2]^{2-}$. The weak interaction energy is calculated at this level of theory to be 11.3 $kJ\,mol^{-1}$ for one coordination side, see Figure 7. Furthermore, as it can be seen for the optimized structure the aforementioned σ-hole points in the direction of the lateral sides (distance 369.8 pm) leading to a distortion of the dimer structure into C_{2h} symmetry, see also Supporting Information. Note, as expected no interaction energy is found at the HF level. This kind of interaction is, however, only possible for the square-planar configuration of $[Cl(I_2)_4]^-$ (Figure 8). An interaction of tetrahedral units would lead to a three-dimensional network which would suffer from steric repulsion of the complex anions and, furthermore, the resulting voids in the network would be too small to accommodate the large countercations, and they would not allow for an interaction of the cations with each other. Cation–cation interactions certainly favor a layer structure which can be realized easily with square-planar $[Cl(I_2)_4]^-$.

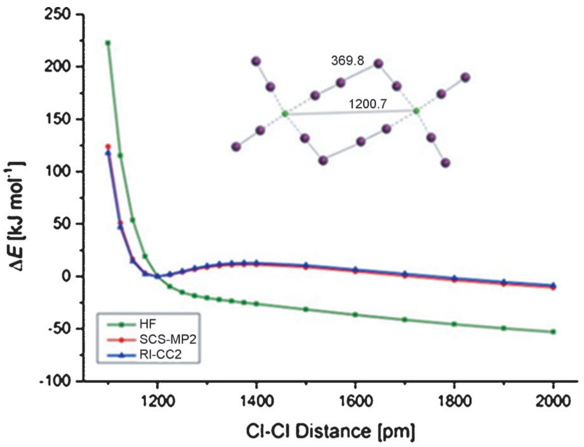

Figure 7. Potential energy scan of the Cl–Cl distance in the $[Cl(I_2)_4]^-$ dimer at different levels of theory using the def2-TZVPP basis-set. The optimized structure of the dimer was set to zero potential. The square-planar structure is not a minimum structure and neither is the dimer.

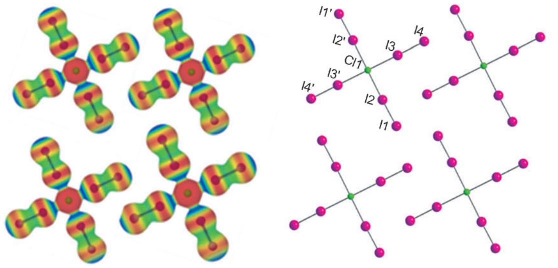

Figure 8. The arrangement of the $[Cl(I_2)_4]^-$ ions in the crystal structure with their electrostatic potentials.

We also analyzed the bonding situation by natural bond order (NBO) and Wiberg bond indices and computed the natural charge (natural population analysis; NPA) of the anion in its tetrahedral and square-planar form. As expected, the central chloride atom is donating charge into the LUMO of the coordinated I_2 units, see Supporting Information for more details. This is also in line with the results of the NPA charges where both structures show the most negative atom to be the central chloride anion (-0.486 (T_d), -0.533 (D_{4h})), whereas the inner iodine atom is almost neutral with a value of 0.053 in both structures. The outer iodine atom is negatively charged by -0.182 (T_d) and -0.170 (D_{4h}), see Supporting Information. The intramolecular bonding situation is therefore similar to other nona-halide systems.

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