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# A 2D Polychloride Network Held Together by Halogen–Halogen Interactions

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***Abstract:*** *In a eutectic mixture of two ionic liquids, we have synthesized and crystallized the new polychloride compound* $[Et_4N]_2[(Cl_3)_2{\cdot}Cl_2]$ *that exhibits a periodic 2D polychloride network acting as an anionic layer. Based on its low melting point and vapor pressure, this compound can be described as a room-temperature ionic liquid. The compound was fully characterized by IR and Raman spectroscopy as well as single-crystal X-ray structure determination. The characterization was complemented by solid-state quantum-chemical calculations confirming the results of the experimental work.*

The chemistry of polyhalide anions is a field of great variety, and has been known for more than a hundred years. For a long time the only known polyhalides were polyiodides.[1] Later also the tribromide $[Br_3]^-$ and the trichloride $[Cl_3]^-$ were first predicted and then characterized.[2] In recent years the field of polyhalide chemistry has caught much attention, especially in the field of polybromides, with new monoanions such as $[Br_9]^-$ or $[Br_{11}]^-$[3–5] and dianions such as $[Br_{20}]^{2-}$.[6,7] Additionally to their use as halogenating agents,[8] these compounds have a great potential for application as ionic liquids (IL) or electrolytes in redox flow batteries.[9] Like these polybromides, polychlorides exhibit a potential application as easy-to-handle chlorinating agents. The fact that chlorine is used during the synthesis or is contained in 55 % of industrial produced chemicals emphasizes the importance of polychloride chemistry.[10]

It is therefore surprising that the chemistry of the lighter halogens is less developed and thus less comprehensive. In the case of chlorine, the only known structure beside $[Cl_3]^-$ is $[Cl_3{\cdots}Cl_2]^-$ characterized by Taraba and Zak in 2003.[11] In the crystal, this anion consists of a $[Cl_3]^-$ anion with a weakly coordinated $Cl_2$ molecule forming an irregularly shaped "hockey-stick"-like motif ($C_s$). This differs from quantum-chemical calculations of isolated $[Cl_5]^-$, which predict a regular V-shaped equilibrium structure ($C_{2v}$) similar to that observed in the crystal structures of the related pentahalides of bromine and iodine.[12] On the other hand, quantum-chemical calculations of isolated $[F_5]^-$ at coupled-cluster level predict the "hockey-stick"-like motif to be marginally more stable.

In any case, in a recently published matrix-isolation investigation at cryogenic conditions, the $[F_5]^-$ was characterized for the first time, showing a regular V-shaped structure.[13] Beyond this observation the smaller polyfluoride anion $[F_3]^-$ was also characterized under cryogenic conditions in noble-gas matrices.[14]

Herein we report the synthesis of a higher polychloride salt $[Et_4N]_2[(Cl_3)_2{\cdot}Cl_2]$. The $[Cl_3]^-$ and $Cl_2$ units form a layered structure, which can be best described as an infinite polychloride network. The compound was crystallized from a eutectic mixture of the ionic liquids *N*-butyl-*N*-methylpyrrolidinium chloride [BMP]Cl and *N*-butyl-*N*-methylpyrrolidinium triflate [BMP]OTf, which was additionally treated with the salt $[Et_4N]Cl$. In principle, this synthesis is a similar approach to the synthesis of $[Br_{20}]^{2-}$ published by Feldmann et al.[6] The combination of the two ionic liquids leads to a melting point drop to approximately 0 °C, which is significantly lower compared to the melting points of the pure ILs ([BMP]Cl 124 °C, [BMP]OTf 4 °C). Additional supply of $[Et_4N]Cl$ and especially $Cl_2$ leads to a further drop beneath −30 °C. For [BMP]OTf and [BMP]Cl, the chlorine solubility was determined to 3.6 wt. % (13.1 mol %) and 33.9 wt. % (56.1 mol %), respectively. The way better solubility of chlorine in the latter is due to the formation of polychloride anions (see Raman spectrum in the Supporting Information, Figure S1). If the reaction mixture of [BMP]Cl, [BMP]OTf, $[Et_4N]Cl$, and $Cl_2$ is cooled beneath −15 °C $[Et_4N]_2[(Cl_3)_2{\cdot}Cl_2]$ crystallizes as colorless plate-shaped crystals. Above −9 °C, the crystals start dissolving again.

The crystal structure was determined by single-crystal X-ray diffraction, showing that the polychloride anions form layers with the cations situated in between (Figures 1 and 2). The salt $[Et_4N]_2[(Cl_3)_2{\cdot}Cl_2]$ crystallizes in the monoclinic space group *C*2/*m*. Like other polyhalides, the structure consists of three different building blocks: $Cl^-$ and $[Cl_3]^-$ as Lewis bases and $Cl_2$ as Lewis acid. A central $Cl^-$ (5) and one bridging $Cl_2$ unit in two differing crystallographic positions form a linear chain. The bond lengths of the coordinated chlorine molecules (1–1′ and 8–8′) are only slightly elongated by 5 pm compared to that found in the crystal structure of $Cl_2$ (199.4(2) pm).[15] This is already known from coordinated $Cl_2$ units.[11] An additional $Cl_2$ unit (6–7) is coordinating end-on; that is, orthogonally to the chain. This coordination is much stronger (255.7(6) pm) than for the bridging units and we may indeed consider this as a distorted $[Cl_3]^-$ anion (β-$Cl_3$). The bond lengths between this $[Cl_3]^-$ group and the two coordinated $Cl_2$ molecules are 301.9(1) pm and 291.9(5) pm,

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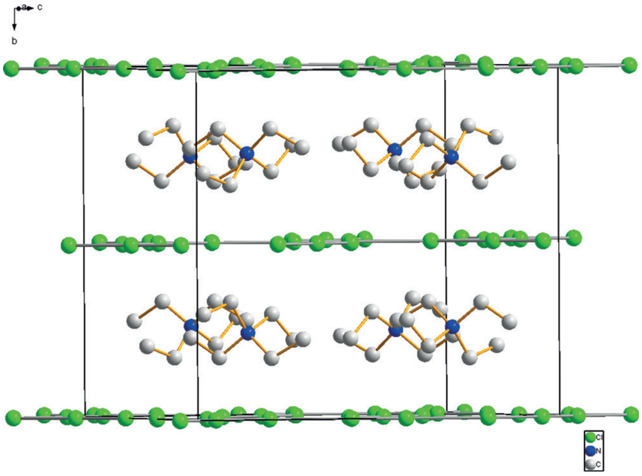


**Figure 1.** Crystal structure of $[Et_4N]_2[(Cl_3)_2{\cdot}Cl_2]$ shown along the *a*-axis.

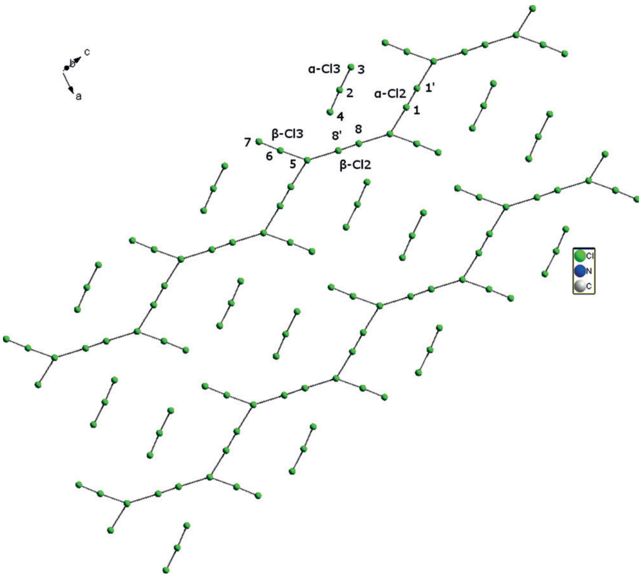


**Figure 2.** Structure of the anionic layer of $[Et_4N]_2[(Cl_3)_2\ Cl_2]$ in the crystal (ellipsoids set at 50% probability). Selected bond lengths [pm] and angles [°]: $r_{56}$ 255.8(3), $r_{67}$ 211.0(3), $r_{23}$ 223.2(2), $r_{24}$ 234.6(2), $r_{11'}$ 202.3(3), $r_{88'}$ 203.7(4), $r_{15}$ 301.9(2), $r_{58}$ 292.0(3); $\alpha_{567}$ 177.4(2), $\alpha_{423}$ 176.5(1).

respectively, and so considerably longer than normal Cl–Cl bonds, but still noticeably shorter than the sum of the van der Waals radii (350 pm).[16] The parallel chains are stacked to planar layers. Embedded within the planar layers, we find an additional $[Cl_3]^-$ group (α-$Cl_3$). This does not show any coordinating contacts to the chlorine framework, and in contrast to the others an almost perfect symmetry of the bond lengths with a disturbance of only 11.4 pm. From all five known crystal structures containing the $[Cl_3]^-$ anion, this is the most symmetric.[17]

Structure optimization of the internal coordinates (fixed unit cell) at DFT level using the B3LYP functional in combination with dispersion correction (D2 according to Grimme)[18] was used to verify the structure determination from the above discussed X-ray diffraction data, simulate IR and Raman spectra, and further analyze the bonding character in the polychloride layers. Counterions were neglected because their influence on the properties of the polychloride network is expected to be minor.

A comparison of the most relevant bond distances and angles shows that the result from the B3LYP-D2 structure optimization agrees well with the experimental structure shown above (Table 1). Most bond distances are well reproduced, with deviations of less than 1 pm. Only the very weak interactions between the $Cl_2$ and $[Cl_3]^-$ ion in the $Cl_3$–$Cl_2$ chains appear to be overestimated, leading to distances that are too small, an effect which is very likely related to the well-known exaggeration of dispersion effects by the D2 correction method in solids.[19]

**Table 1:** Calculated and experimental structure parameters.[a]

| Compound | X-Ray | B3LYP-D2 | Fragment |
|---|---|---|---|
| $r_{11'}$ | 202.3(3) | 207.4 | α-$Cl_2$ |
| $r_{88'}$ | 203.7(4) | 211.2 | β-$Cl_2$ |
| $r_{56}$ | 255.8(3) | 243.6 | β-$Cl_3$ |
| $r_{67}$ | 211.0(3) | 219.7 | β-$Cl_3$ |
| $r_{23}$ | 223.2(2) | 228.5 | α-$Cl_3$ |
| $r_{24}$ | 234.6(2) | 231.2 | α-$Cl_3$ |
| $r_{15}$ | 301.9(2) | 294.7 | |
| $r_{85}$ | 292.0(3) | 280.1 | |
| $\alpha_{567}$ | 177.4(2) | 179.1 | β-$Cl_3$ |
| $\alpha_{423}$ | 176.5(1) | 179.8 | α-$Cl_3$ |

[a] Bond lengths in pm and angles in degrees.

Comparison with calculations for isolated $Cl_2$ ($r = 200.4$ pm) and $[Cl_3]^-$ ($r = 230.3$ pm) molecules at the same level of theory show that the two $Cl_2$-like and the isolated $Cl_3$-like molecules (α-$Cl_3$) in the polychloride layer are only slightly perturbed from their equilibrium structure in vacuum. The second $Cl_3$-like molecule (β-$Cl_3$) is much more perturbed and appears to resemble an intermediate between $[Cl_3]^-$ and a $Cl_2$ bound to a $Cl^-$. Such bonding situations can be further investigated by vibrational spectroscopy. Raman spectroscopy in particular is a very powerful technique, as the present system shows a strong Raman-scattering effect (Figure 3).

The measured Raman spectrum shows a strong band at 280 $cm^{-1}$ (calc. 277 $cm^{-1}$) belonging to the symmetric stretching vibration of the $[Cl_3]^-$ ion. This is in good agreement with the bands observed in our previous powder spectra of $[Et_4N]^+[Cl_3{\cdots}Cl_2]^-$ (274 $cm^{-1}$) and $[Pr_4N]^+[Cl_3]^-$ (272 $cm^{-1}$).[12] Another intense broad Raman band centered at 465 $cm^{-1}$ (calc. 454 $cm^{-1}$) is assigned to the stretching mode of one $Cl_2$ unit.[11,12] Furthermore, we found a less intense Raman band at 420 $cm^{-1}$ (calc. 424 $cm^{-1}$) that can be assigned to the Cl–Cl stretching mode of the other $Cl_2$ unit. At 350 $cm^{-1}$ and 313 $cm^{-1}$, two bands with lower intensity occur belonging to the triflate anion,[20] which was part of the ionic liquids used as solvents. The large band below 100 $cm^{-1}$ belongs to longitudinal vibrations of the compound. Along with the Raman spectrum, a far-IR spectrum was measured (Figure 4 and Table 2). The spectrum shows two broad bands

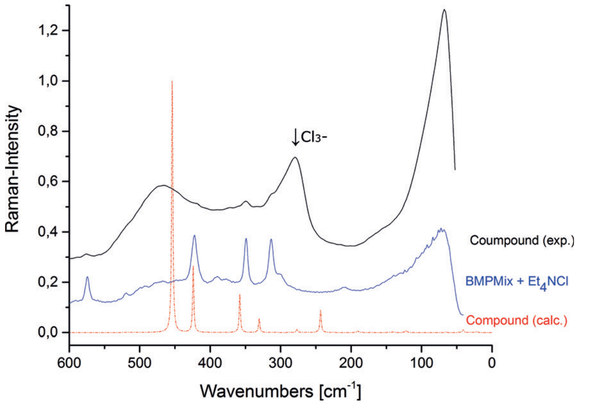


***Figure 3.*** Experimental (——) and at B3LYP-D2 level calculated Raman spectrum (-----).

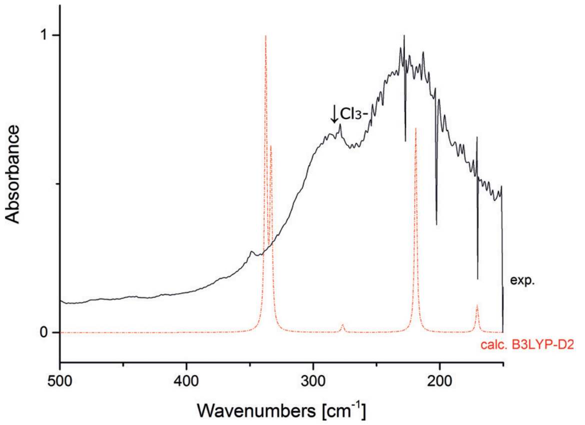


***Figure 4.*** Experimental (——) and at B3LYP-D2 level calculated IR spectrum (-----).

***Table 2:*** Experimental and computed vibrational frequencies.

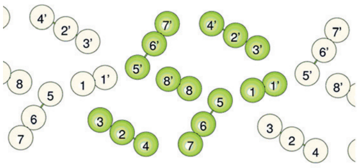
| Mode[a] | Experimental Raman[b] | Experimental IR | Calculated Raman[c] | Calculated IR[c] | Ref.[11,16] |
|---|---|---|---|---|---|
| $\nu_s$ $[Cl_3]^-$ | | 228.5 | | 219.1 | 232 |
| $\nu_1$ $[Cl_3]^-$ | 279.8 | 278.6 | 278.7 | 276.8 | 275 |
| $2\nu_2$ $[Cl_3]^-$ | 333.2 | | 330.4 | 333.3 | 330 |
| $\nu_s$ $[Cl_3\cdots Cl_2]^-$ | | | 358.0 | 337.4 | |
| $\nu_1$ $[Cl_3\cdots Cl_2]^-$ | 420.3 | | 424.1 | | |
| $\nu_1$ L-sh | 465.7 | | 453.8 | | 466 |

[a] Frequencies in cm$^{-1}$. [b] calculated band at 358 probably overlain by $[OTf]^-$ band. [c] calculated at B3LYP-D2 level.

of the symmetric and antisymmetric stretching mode of $[Cl_3]^-$ at 277 and 228 cm$^{-1}$, respectively.[21]

A general problem regarding reactions of organic substances and elemental chlorine is partial chlorination of the organic cation. To assure that unwanted chlorination of the cation does not occur, an NMR spectrum of the eutectic mixture was recorded after the addition of $Cl_2$. Signals indicating chlorination of the cation were not observed (Supporting Information, Figure S2).

For a qualitative characterization of the bonding pattern in the Cl layers, Mulliken charges were calculated from the Hartree–Fock wave function taking into account the experimental crystal structure (Figure 5). The entire unit cell of the isolated Cl network has a charge of −4 a.u. The network consists of stronger bound $Cl_3$–$Cl_2$ chains with Mulliken charges of −0.990 and −0.090/−0.136 a.u., respectively, and looser bound $[Cl_3]^-$ ions with a Mulliken charge of −0.998 a.u. For further analysis, the electrostatic potential was calculated within the plain. Figure 6 shows a combined contour-rainbow plot of the electrostatic potential with one additional (bold) contour indicating the electron density value of 0.001 e bohr$^{-3}$, which is the value suggested by Bader et al. for exploring features in the electrostatic potential around a molecule.[22] Most remarkable in this map are the regions of less negative potentials along the extension of the bond axis in the α-$Cl_3$ units (known as σ-holes) and the related belts of negative potential perpendicular to the bond axis at both lateral chlorine atoms. The atoms within the $Cl_2$–$Cl_3$ chains are too close to each other to observe σ-holes, but the belts are visible to less extent for the β-$Cl_2$ and β-$Cl_3$ units as well. Thus one also observes a weak σ-hole interaction between β-$Cl_2$ and α-$Cl_3$ units, as well as between the β-$Cl_3$ and α-$Cl_3$ units. These



| | | |
|---|---|---|
| 1 | −0.045 | α-$Cl_2$ |
| 2 | −0.021 | α-$Cl_3$ |
| 3 | −0.415 | |
| 4 | −0.562 | |
| 5 | −0.658 | β-$Cl_3$ |
| 6 | −0.009 | |
| 7 | −0.222 | |
| 8 | −0.068 | β-$Cl_2$ |

***Figure 5.*** Computed Mulliken charges of the polychloride network calculated for the experimental structure at the HF level.

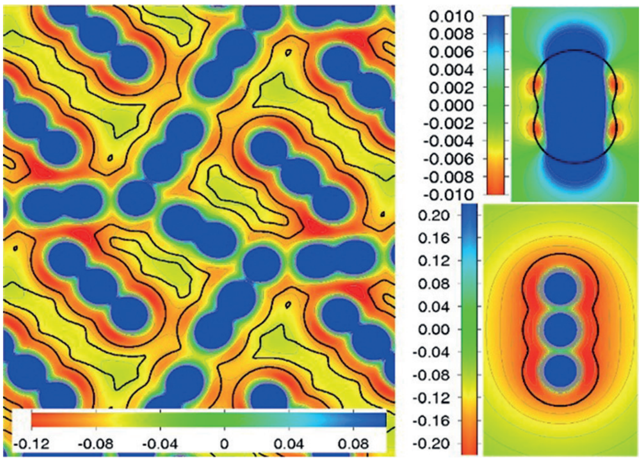


***Figure 6.*** Plot of the electrostatic potential (in a.u.) of the polychloride network as well as for the isolated $Cl_2$ and $[Cl_3]^-$ molecules. The bold black line indicates the electron density contour line of 0.001 e bohr$^{-3}$. Thin gray contours show equi-electostatic potentials as indicated in the color bar with intervals of 0.02 (Cl layer, $[Cl_3]^-$) and 0.002 a.u. ($Cl_2$).

halogen–halogen interactions lead to further stability of the negatively charged polychloride network.

In conclusion, we report the synthesis and full characterization of the first higher polychloride network prepared from a eutectic mixture of ionic liquids. The 2D network is best described as a $[Et_4N]_2[(Cl_3)_2{\cdot}Cl_2]$ salt in which a polychloride layer out of $[Cl_3]^-$ and $Cl_2$ units is formed. The nature of the chemical bond between these units can be understood as halogen-halogen bonding which is in agreement with quantum-chemical calculations. As the reported compound exhibits a melting point around −9 °C and a low chlorine vapor pressure, the system can be described as a room-temperature ionic liquid.

## Experimental Section

All of the preparative work was carried out using standard Schlenk techniques. The ionic liquids [BMP]Cl and [BMP]OTf were dried in vacuum for 2 days at 50 °C and used without further purification. The $Cl_2$ gas was passed through $CaCl_2$ to remove traces of $H_2O$ before use. [BMP]Cl and [BMP]OTf were purchased from IoLiTec, the $Cl_2$ gas used was of 2.5 purity from Linde Gas, and $[Et_4N]Cl$ was used as ordered from AppliChem. The Raman spectra were recorded on a Bruker MultiRAM II equipped with a low-temperature Ge-detector (1064 nm, 50 mW, resolution 1 $cm^{-1}$); the IR-spectra was measured on a Bruker Vertex 80v spectrometer with a far-IR-DTGS detector (resolution 2 $cm^{-1}$).

[BMP]Cl (773 mg; 4.4 mmol) and [BMP]OTf (1320 mg; 4.4 mmol) were mixed in a Schlenk tube flushed with argon and stirred for 1 h until a milky white viscous liquid formed. After addition of $[Et_4N]Cl$ (270 mg; 2.2 mmol), which remained insoluble, $Cl_2$ gas was passed through the tube. Upon contact with the $Cl_2$ gas, the color of the mixture turned from colorless to bright yellow and the turbid liquid cleared. After passing the $Cl_{2(g)}$ through the tube for about 5 min the ammonium salt started dissolving in the yellow liquid, forming a clear bright yellow solution. After the $[Et_4N]Cl$ was fully dissolved, $Cl_{2(g)}$ was passed through the reaction mixture for another circa 5 min. Then the vessel was closed and stirred at room temperature overnight. At the next day the tube was stored at −20 °C. After 5 days small colorless plate-shaped crystals formed.

Crystal data for $[NEt_4]_2[Cl_8]$: $C_8H_{20}Cl_4N$, $M_w = 272{,}05$, monoclinic, space group $C2/m$, $a = 1448.2(2)$ pm, $b = 1270.2(1)$ pm; $c = 1500.4(1)$ pm, $\beta = 102.3(1)°$, $V = 2696.3(3) \times 10^6$ pm$^3$, $Z = 8$, $\rho_{calc} = 1{,}340$ gcm$^{-3}$, F(000) = 1144, $\lambda = 0.71073$ Å, $T = 100(2)$ K, absorption coefficient = 0.841 mm$^{-1}$, absorption correction: multi-scan, $T_{min} = 0.6398$, $T_{max} = 0.7454$. Data for the structure were collected on a Bruker D8 Venture CMOS area detector diffractometer with Mo-$K_\alpha$ radiation. A single crystal was coated at −25 °C with perfluoroether oil and mounted on a 0.1 mm Micromount. The structure was solved by direct methods in SHELXTL[23] and refined by least squares on weighted $F^2$ values for all reflections using OLEX2.[24] The final refinements converged at GooF = 1.162, $R1 = 0.0672$, and $wR2 = 0.1511$ for all reflections ($I > 2\sigma(I)$). The hydrogen atoms were included in the refinement in calculated positions by a riding model. The graphical representations were prepared with Diamond.[25] CCDC 1416833 contains the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre.

Computational details: Periodic Hartree–Fock (HF) and density functional theory (DFT) calculations based on the experimental single-crystal polychloride structures (the counterions were neglected) were performed. An energy-consistent, multi-electron fit, quasi relativistic Stuttgart–Cologne pseudo potential with a chemically inactive [Ne] core was utilized.[26] The valence electrons were represented by a triple-ζ basis set that in a previous investigation of solid chlorine[27] was derived from a (6s6p)/[3s3p] basis set by Dolg[28] (for details about this basis set and its derivation, see Ref. [27] and corresponding Supporting Information). All calculations were performed with the Crystal14 program.[29] All DFT structure optimizations made use of dispersion correction according to Grimme's D2 scheme[18] as implemented in the Crystal14 program.[30] A 6 × 6 × 6 Monkhorst-Pack grid for $k$-space sampling and truncation criteria for 2-electron integrals (thresholds for the overlap of atomic orbitals from pairs of atoms, which determine if Coulomb or exchange integrals are evaluated or not; TOLINTEG, cf. Crystal14 manual[25]) of $10^{-10}$, $10^{-10}$, $10^{-10}$, $10^{-20}$, and $10^{-50}$ were chosen.

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