

# Synthesis of a Hexachloro Sulfate(IV) Dianion Enabled by Polychloride Chemistry

Patrick Voßnacker, Alisa Wüst, Carsten Müller, Merlin Kleoff, and Sebastian Riedel\*

In memory of Professor Ralf Steudel

**Abstract:** The preparation and structural characterization of  $[\text{NET}_3\text{Me}]_2[\text{SCl}_6]$  is described, which is the first example of a  $[\text{SCl}_6]^{2-}$  dianion and of a halosulfate anion of the type  $[\text{S}_x\text{X}_y]^{z-}$  in general. This dianion belongs to the group of 14-valence electron  $\text{AB}_6\text{E}$  systems and forms an octahedral structure in the solid-state. Interestingly, co-crystallization with  $\text{CH}_2\text{Cl}_2$  affords  $[\text{NET}_3\text{Me}]_2[\text{SCl}_6] \cdot 4\text{CH}_2\text{Cl}_2$  containing  $[\text{SCl}_6]^{2-}$  dianions with  $C_{4v}$  symmetry. As suggested by quantum-chemical calculations, the distortion of the structure is not caused by a stereochemically active lone pair but by enhanced hydrogen bonding interactions with  $\text{CH}_2\text{Cl}_2$ . At elevated temperatures,  $[\text{NET}_3\text{Me}]_2[\text{SCl}_6]$  decomposes to various sulfur chlorine compounds as shown by Raman spectroscopy. Cooling back to room temperature results in the selective formation of  $[\text{NET}_3\text{Me}]_2[\text{SCl}_6]$  which is comparable to the well-studied  $\text{SCl}_4$ .

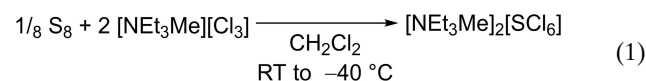
The chlorination of small molecules is a topic of major relevance both for industrial and academic research.<sup>[1]</sup> Very recently, our group in cooperation with Covestro investigated  $[\text{NET}_3\text{Me}]\text{Cl}$  as a practical chlorine storage medium which forms the corresponding trichloride  $[\text{NET}_3\text{Me}][\text{Cl}_3]$  by addition of chlorine.<sup>[2]</sup> More importantly, we found that  $[\text{NET}_3\text{Me}][\text{Cl}_3]$  is also a useful chlorinating agent reacting with carbon monoxide to the base chemical phosgene ( $\text{COCl}_2$ ). Interestingly, our studies indicate that the trichloride anion in  $[\text{NET}_3\text{Me}][\text{Cl}_3]$  has a Cl–Cl bond which is much weaker than in elemental chlorine facilitating the insertion of carbon monoxide into the Cl–Cl bond of the trichloride.<sup>[3]</sup>

In contrast to elemental chlorine,  $[\text{NET}_3\text{Me}][\text{Cl}_3]$  contains the chemically inert cation  $[\text{NET}_3\text{Me}]^+$  which has proven to be very useful to stabilize various reactive anions.<sup>[4]</sup> Therefore, we speculated that the exceptional ability of

$[\text{NET}_3\text{Me}][\text{Cl}_3]$  to serve both as a strong chlorination reagent and to form stable salts with unique anions would enable the preparation of unknown chlorine-containing compounds. While focusing on sulfur compounds, we noted that most sulfur chlorides are relatively unstable species. Reaction of elemental sulfur with chlorine leads primarily to  $\text{S}_2\text{Cl}_2$ , which can be further reacted with an excess of chlorine in the presence of  $\text{FeCl}_3$  as catalyst to  $\text{SCl}_2$ .<sup>[5]</sup> While  $\text{S}_2\text{Cl}_2$  is comparably stable,  $\text{SCl}_2$  decomposes at room temperature slowly to  $\text{S}_2\text{Cl}_2$  and  $\text{Cl}_2$ . At  $-78^\circ\text{C}$ ,  $\text{SCl}_2$  reacts with liquid  $\text{Cl}_2$  to  $\text{SCl}_4$  but decomposes to  $\text{SCl}_2$  and  $\text{Cl}_2$  when warmed above its melting point of  $-30^\circ\text{C}$ . Below that temperature,  $\text{SCl}_4$  exists in the ionic structure  $[\text{SCl}_3]^+[\text{Cl}]^-$ , as suggested by IR and Raman spectroscopy and powder XRD analysis.<sup>[6]</sup> Beside  $\text{SCl}_4$ , various salts of the type  $[\text{SCl}_3]^+[\text{X}]^-$  with, e.g.,  $\text{X} = [\text{ICl}_4]$ ,<sup>[7]</sup>  $[\text{SbF}_6]$ ,<sup>[8]</sup>  $[\text{F}(\text{Al}(\text{OC}_4\text{F}_9)_3)_2]$ <sup>[9]</sup> have been prepared. The highest possible binary sulfur chlorine species,  $\text{SCl}_6$ , is not known, while the lighter homologue  $\text{SF}_6$  is a stable compound that found various industrial applications.<sup>[10]</sup> Surprisingly, chlorosulfates,  $[\text{S}_x\text{Cl}_y]^{z-}$ , have not been prepared thus far, although afterglow-tandem mass spectrometric experiments gave a  $D_0(\text{SCl}_2-\text{Cl}^-)$  bond energy of  $85 \pm 8 \text{ kJ mol}^{-1}$  for the  $[\text{SCl}_3]^-$  which is in the same range as the bond energy within the  $[\text{Cl}_3]^-$  anion ( $99 \pm 5 \text{ kJ mol}^{-1}$ ).<sup>[11]</sup> In contrast, for the heavier elements Se and Te a plethora of chloroselenates and chlorotellurates in the oxidation states II and IV are known for decades (e.g.,  $[\text{Se}_2\text{Cl}_6]^{2-}$ ,<sup>[12]</sup>  $[\text{Se}_4\text{Cl}_{12}]^{2-}$ ,<sup>[13]</sup>  $[\text{ChCl}_6]^{2-}$ ,<sup>[14]</sup>  $[\text{Ch}_2\text{Cl}_{10}]^{2-}$ ,<sup>[13,15]</sup>  $[\text{Ch}_3\text{Cl}_{13}]^{16}$  ( $\text{Ch} = \text{Se}, \text{Te}$ )).

At the outset, we prepared the ionic liquid  $[\text{NET}_3\text{Me}][\text{Cl}_3]$  by the reaction of commercially available  $[\text{NET}_3\text{Me}]\text{Cl}$  with elemental chlorine as previously described.<sup>[3]</sup>

A solution of  $[\text{NET}_3\text{Me}][\text{Cl}_3]$  in  $\text{CH}_2\text{Cl}_2$  was reacted with elemental sulfur at room temperature for 16 h [Eq. (1)]. Slowly cooling to  $-40^\circ\text{C}$  yielded yellow crystals that could be analyzed by X-ray diffraction revealing the formation of  $[\text{NET}_3\text{Me}]_2[\text{SCl}_6]$  (Figure 1, left).



In this structure, the  $[\text{SCl}_6]^{2-}$  dianion has an almost octahedral geometry with S–Cl bond lengths of 231.2(1), 231.5(1) and 232.3(1) pm and bond angles between 88.9(1)° and 91.1(1)°. The  $[\text{SCl}_6]^{2-}$  dianion is stabilized by weak

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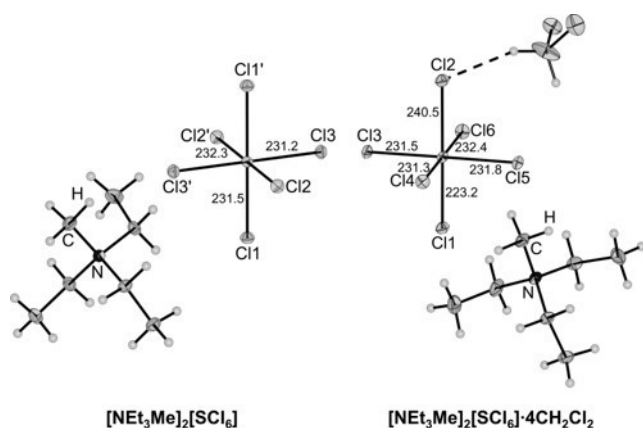
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**Figure 1.** Molecular structure of  $[\text{NEt}_3\text{Me}]_2[\text{SCl}_6]$  (left) and  $[\text{NEt}_3\text{Me}]_2[\text{SCl}_6]\cdot 4\text{CH}_2\text{Cl}_2$  (right) in the solid state with thermal ellipsoids shown at 50% probability. Bond lengths are given in pm with an error of 0.1 pm.

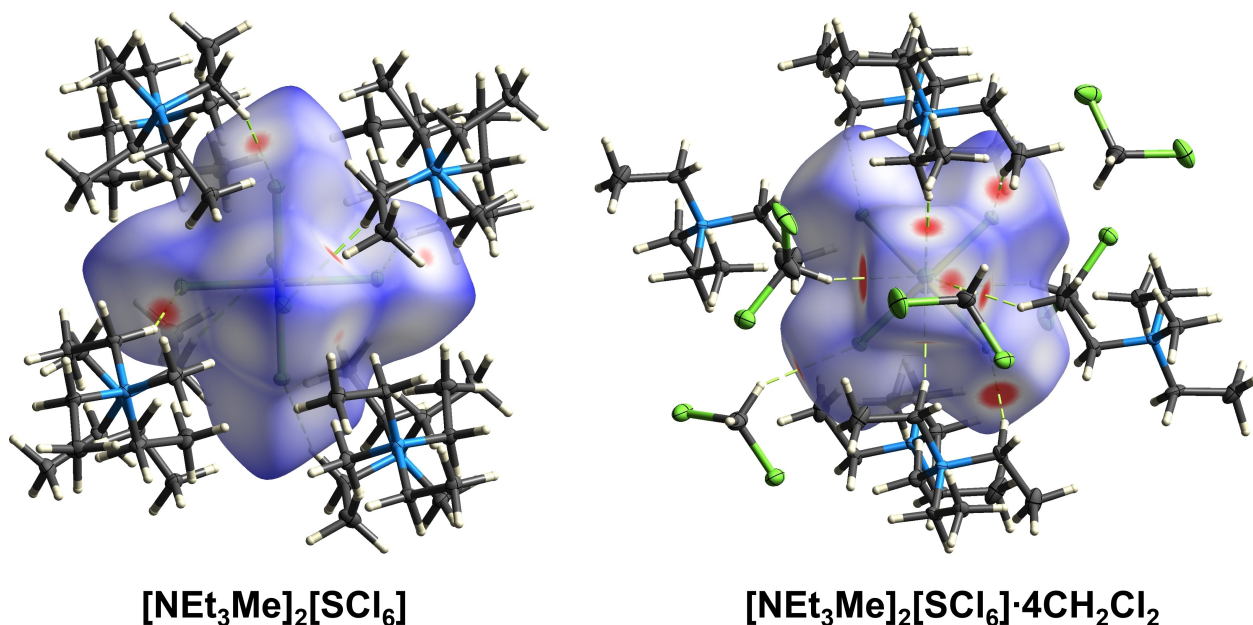
hydrogen bonding interactions between the  $[\text{NEt}_3\text{Me}]^+$  cation and the dianion (see Figure 2). The Raman spectrum of a single crystal of  $[\text{NEt}_3\text{Me}]_2[\text{SCl}_6]$  further indicated an octahedral geometry for the  $[\text{SCl}_6]^{2-}$  dianion showing only three bands at 282, 241, and 168  $\text{cm}^{-1}$  in the region for S–Cl vibrations (See Figure S4). These bands can be assigned to the  $A_{1g}$  and  $E_g$  symmetric S–Cl stretching vibrations and the  $T_{2g}$  symmetric bending vibration, respectively, and are in agreement with the vibrational spectra calculated at Cosmo-SCS-MP2/def2-TZVPP level of theory (see Figure S3).

When a diluted solution of  $[\text{NEt}_3\text{Me}][\text{Cl}_3]$  and sulfur in  $\text{CH}_2\text{Cl}_2$  was cooled to  $-80^\circ\text{C}$ , co-crystallization of  $\text{CH}_2\text{Cl}_2$  with  $[\text{NEt}_3\text{Me}]_2[\text{SCl}_6]$  was observed. Surprisingly, X-ray

diffraction of the obtained crystals of  $[\text{NEt}_3\text{Me}]_2[\text{SCl}_6]\cdot 4\text{CH}_2\text{Cl}_2$  revealed a different structure for the  $[\text{SCl}_6]^{2-}$  dianion (Figure 1, right). Compared to the previously analyzed structure, the S–Cl1 bond is shortened by 8.3(1) pm (compared to the average S–Cl bond length) while the S–Cl2 bond is significantly elongated by 8.8(1) pm. Therefore, the octahedral symmetry of the  $[\text{SCl}_6]^{2-}$  dianion is distorted yielding a  $C_{4v}$  symmetric structure.

In general, the  $[\text{SCl}_6]^{2-}$  dianion belongs to the group of  $\text{AB}_6\text{E}$  systems bearing six ligands and one lone pair. According to the valence shell electron pair repulsion model (VSEPR), these systems should possess a stereochemically active lone pair and form structures of distorted octahedral geometries. However, the prediction of the VSEPR model is not always correct for these systems. Consequently, they have received significant attention over the last decades both from an experimental and a theoretical point of view.<sup>[17–19]</sup> For  $\text{XeF}_6$ ,<sup>[20]</sup>  $[\text{IF}_6]^-$ ,<sup>[21]</sup> and  $[\text{SeF}_6]^{2-}$ ,<sup>[22]</sup> a distorted octahedral structure with  $C_{3v}$  symmetry is observed, while, for instance,  $[\text{ClF}_6]^-$ <sup>[23]</sup> and  $[\text{BrF}_6]^-$ <sup>[22,24]</sup> have octahedral structures. For the higher homologues of  $[\text{SCl}_6]^{2-}$ ,  $[\text{SeCl}_6]^{2-}$ ,<sup>[25]</sup> and  $[\text{TeCl}_6]^{2-}$ <sup>[26]</sup> both regular and distorted octahedral structures were found depending on the corresponding cation.

These examples demonstrate that both structures can be formed by  $\text{AB}_6\text{E}$  systems. In the literature, two contrary effects are discussed that have to be taken into account. The first effect is that the system can be stabilized in principle when the HOMO and the LUMO are interacting. However, this combination is prohibited in  $O_h$  symmetry due to different irreducible representations of the HOMO ( $A_{1g}$ ) and the LUMO ( $T_{1u}$ ). When the octahedral structure is distorted, HOMO–LUMO interaction is allowed resulting in



**Figure 2.** Hirshfeld surface of  $[\text{NEt}_3\text{Me}]_2[\text{SCl}_6]$  (left) and  $[\text{NEt}_3\text{Me}]_2[\text{SCl}_6]\cdot 4\text{CH}_2\text{Cl}_2$  (right). Disorders are omitted for clarity. Color code: blue = N, grey = C, white = H, yellow = S, green = Cl. Dashed green lines display hydrogen bonds.

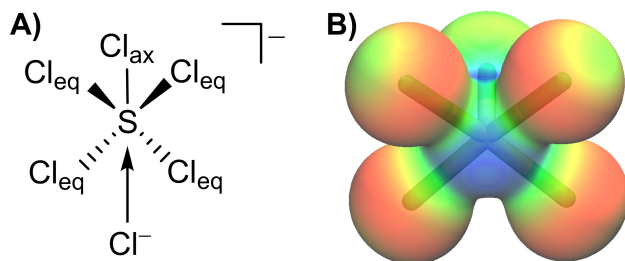
a stabilization of the system, also known as a second-order Jahn–Teller effect. For an octahedral structure the lone pair is located in the s orbital of the central atom and therefore stereochemically inactive. Lowering the symmetry increases the p character of the lone pair. It becomes stereochemically active and can be located at the plane ( $C_{3v}$ ), edge ( $C_{2v}$ ), or corner ( $C_{4v}$ ) of the octahedron (see Figure S8), with the former being the generally favored and the latter the least probable possibility. The second, contrary, effect is the electronic repulsion between the ligands making an octahedral structure more favorable. For many systems, there is a delicate balance between the symmetrical octahedral and the distorted structure. Therefore, already weak interactions of the anion with its molecular environment, e.g., by hydrogen bonding to the cation can determine the structure.<sup>[17,18]</sup>

As mentioned above, the distortion from an  $O_h$  symmetry to a  $C_{4v}$  geometry, as found for  $[\text{NEt}_3\text{Me}]_2[\text{SCl}_6] \cdot 4\text{CH}_2\text{Cl}_2$ , is quite unusual. Therefore, an NBO analysis of the distorted  $[\text{SCl}_6]^{2-}$  was performed and revealed that the lone pair of the sulfur is located in the 3s orbital and is stereochemically inactive (see Figure S9).

To further investigate the energetical influence of a distortion of  $[\text{SCl}_6]^{2-}$ , a relaxed surface scan was performed by starting from an octahedral structure and subsequently increasing one S–Cl bond (see Figure S10 to S12). An elongation of the S–Cl2 bond by 10 pm translates to an energetical increase of only  $0.6\text{ kJ mol}^{-1}$ . On the other hand, this distortion leads to an increased negative charge on Cl2 (Natural Charge  $-0.43$  vs.  $-0.49$ ) which enables stronger hydrogen bonding interactions.

Indeed, these interactions are found by Hirshfeld analysis of the solid state structure of  $[\text{NEt}_3\text{Me}]_2[\text{SCl}_6] \cdot 4\text{CH}_2\text{Cl}_2$  (Figure 2). Overall, the Cl2 has five H...Cl interactions below the sum of the van der Waals radii ( $\Sigma_{\text{vdw}}(\text{H}–\text{Cl}) = 285\text{ pm}$ ).

As one of the S–Cl bonds is significantly elongated, the  $[\text{SCl}_6]^{2-}$  species could be described as a  $[\text{SCl}_5]^-$  fragment and a  $\text{Cl}^-$  anion. In this description, the  $[\text{SCl}_5]^-$  species consists of four equatorial S–Cl bonds formed by 3-center-4-electron bonds and one axial S–Cl bond which is a classical 2-center-2-electron bond (Figure 3A). Therefore, we calculated the electrostatic potential of  $[\text{SCl}_5]^-$  and mapped it onto the

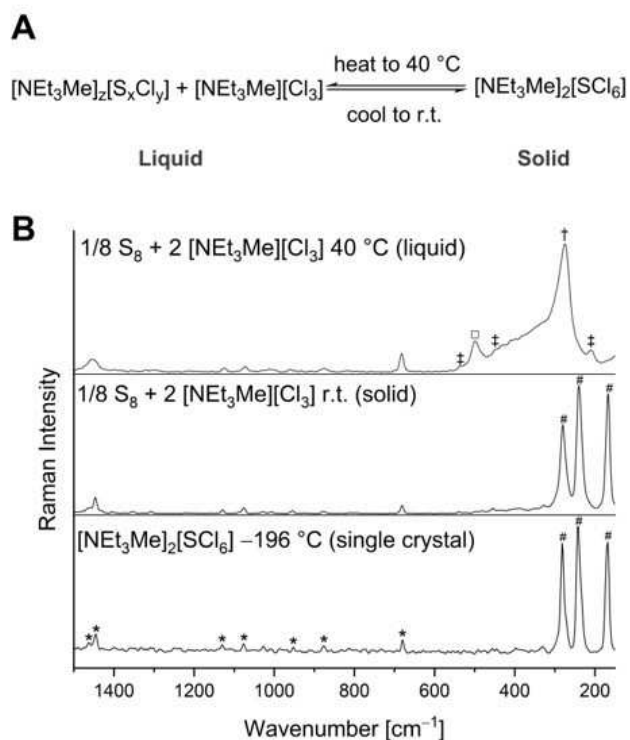


**Figure 3.** A) Interaction of  $\text{Cl}^-$  with the  $\sigma$ -hole of  $[\text{SCl}_5]^-$  formally forming  $[\text{SCl}_6]^{2-}$ . B) Electrostatic potential of  $[\text{SCl}_5]^-$  in a range of:  $-0.15$  (red) to  $0.05$  a.u. (blue) mapped onto the electron density (isosurface value  $0.025$  a.u.) calculated on B3LYP-D4/def2-TZVPP level of theory.

electron density (Figure 3B). According to these calculations, there is a high negative charge located on the equatorial Cl atoms while a more positive electrostatic potential can be found on the central sulfur atom along the S–Cl<sub>ax</sub> bond, the so called  $\sigma$ -hole. Thus, the  $\text{Cl}^-$  can interact with this positively charged region of the  $[\text{SCl}_5]^-$  fragment. Additionally, the  $\text{Cl}^-$  can donate electron density into the  $\sigma^*$  orbital (S–Cl<sub>ax</sub>, LUMO) resulting in a weakening and elongation of the S–Cl<sub>ax</sub> bond. This bonding situation is similar to that found in polyhalides.<sup>[27]</sup>

An atoms in molecules (AIM) analysis based on periodic DFT calculations shows an ionic character of the S–Cl interaction in the dianion. At all corresponding bond critical points, the Laplacian is small and positive (ca.  $1.7\text{--}1.8\text{ e \AA}^{-5}$ ), the ratio of the absolute potential ( $|V|$ ) and kinetic energy density ( $G$ ) is below 2.0 (1.6), and the value of the electron localization function (ELF) is only about 0.6—all indicative for a non-shared interaction (see Table S5).

At last, we investigated the influence of the temperature on the formation of  $[\text{NEt}_3\text{Me}]_2[\text{SCl}_6]$  from a stoichiometric mixture of  $\text{S}_8$  and  $[\text{NEt}_3\text{Me}][\text{Cl}_3]$  by Raman spectroscopy (Figure 4). Interestingly, at  $40^\circ\text{C}$  the mixture exists as a liquid consisting of various species including  $[\text{Cl}_3]^-$  and  $\text{S}_2\text{Cl}_2$  as indicated by comparison with reference substances (see Figure S6). In addition, the presence of  $[\text{SCl}_5]^-$  could be



**Figure 4.** A) The thermal equilibrium of  $[\text{NEt}_3\text{Me}]_2[\text{SCl}_6]$  with various sulfur chlorine compounds. B) Raman spectrum of the reaction mixture of sulfur and  $[\text{NEt}_3\text{Me}][\text{Cl}_3]$  at  $40^\circ\text{C}$  (above) and room temperature (middle) and comparison to the Raman spectrum of the single crystal of  $[\text{NEt}_3\text{Me}]_2[\text{SCl}_6]$  (below). Bands are assigned as follows (\* = cation, # =  $[\text{SCl}_6]^{2-}$ , † =  $[\text{Cl}_3]^-$ , ‡ =  $\text{S}_2\text{Cl}_2$ , □ = presumably  $[\text{SCl}_5]^-$ ). See Figure S6 for reference spectra.



assumed as the calculated spectrum at SCS-MP2/def2-TZVPP level of theory is in good agreement with the measured spectrum (see Figure S6). When cooled to room temperature, the mixture solidified and the measured Raman spectrum thereof was consistent with those obtained for the single crystals of  $[\text{NEt}_3\text{Me}]_2[\text{SCl}_6]$  suggesting its selective formation. This highlights that the crystallization of  $[\text{NEt}_3\text{Me}]_2[\text{SCl}_6]$  is energetically highly favored due to its comparably large lattice energy. A rough estimation of the stabilization energy the dianion meets due to the periodic cation-lattice yields about  $240 \text{ kJ mol}^{-1}$  (see Supporting Information, chapter h). When the solidified  $[\text{NEt}_3\text{Me}]_2[\text{SCl}_6]$  is heated to  $40^\circ\text{C}$  again, a similar spectrum is observed as for the reaction mixture. Thus, it can be assumed that there is an equilibrium between various sulfur chlorides in the liquid mixture and  $[\text{SCl}_6]^{2-}$  in the solid (Figure 4A). Given these results, the thermal behavior of  $[\text{NEt}_3\text{Me}]_2[\text{SCl}_6]$  is comparable to  $\text{SCl}_4$ , which is only stable below  $-30^\circ\text{C}$  and decomposes above this temperature to  $\text{SCl}_2$  and  $\text{Cl}_2$ .

In conclusion, we synthesized  $[\text{NEt}_3\text{Me}]_2[\text{SCl}_6]$ , which is the first example of a halosulfate anion of the type  $[\text{S}_x\text{X}_y]^{z-}$ . Additionally, this unprecedented molecule is one of the few examples for a 14-valence electron  $\text{AB}_6\text{E}$  system with a central atom of the third period. In general,  $\text{AB}_6\text{E}$  systems can either adopt an octahedral symmetry or a distorted structure with a stereochemically active lone pair. In  $[\text{NEt}_3\text{Me}]_2[\text{SCl}_6]$ , we found an octahedral symmetry for the  $[\text{SCl}_6]^{2-}$  dianion in the solid-state structure. However, when  $\text{CH}_2\text{Cl}_2$  co-crystallized,  $[\text{NEt}_3\text{Me}]_2[\text{SCl}_6] \cdot 4 \text{CH}_2\text{Cl}_2$  was formed with an unusual  $\text{C}_{4v}$  structure, with one elongated and one shortened axial S–Cl bond. Quantum-chemical calculations revealed that this distortion cannot be attributed to a stereochemically active lone pair but is a result of enhanced hydrogen bonding interactions with  $\text{CH}_2\text{Cl}_2$ .

Notably,  $[\text{NEt}_3\text{Me}]_2[\text{SCl}_6]$  decomposes to various sulfur chlorine compounds at  $40^\circ\text{C}$  while cooling back to room temperature results in the selective formation of  $[\text{NEt}_3\text{Me}]_2[\text{SCl}_6]$  highlighting the similarity to the well-studied  $\text{SCl}_4$ . This work demonstrates the unique ability of  $[\text{NEt}_3\text{Me}][\text{Cl}_3]$  to serve as a versatile chlorination agent while stabilizing unprecedented anions.

## Acknowledgements

We thank Dr. Daniel Franz (FU Berlin) for recording the SCXRD data of  $[\text{NEt}_3\text{Me}]_2[\text{SCl}_6]$  and Prof. Martin Kaupp for fruitful discussions. We would like to acknowledge the assistance of the Core Facility BioSupraMol supported by the DFG, the HPC Service of ZEDAT, Freie Universität Berlin, for computing time and the ERC Project HighPotOx (Grant agreement ID: 818862) for funding. Open Access funding enabled and organized by Projekt DEAL.

## Conflict of Interest

The authors declare no conflict of interest.

## Data Availability Statement

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

**Keywords:** Ionic Liquids · Polychlorides · Quantum Chemistry · Sulfur · VSEPR Model

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Manuscript received: July 2, 2022

Accepted manuscript online: August 4, 2022

Version of record online: August 30, 2022