

Article

The Homopolyatomic Sulfur Cation $[S_{20}]^{2+}$

Janis Derendorf ¹, Lara Heiderich ¹, Carsten Jenne ^{1,*}  and Marc C. Nierstenhöfer ^{1,2} 
¹ Anorganische Chemie, Fakultät für Mathematik und Naturwissenschaften, Bergische Universität Wuppertal, Gaußstr. 20, 42119 Wuppertal, Germany

² Chemische Sicherheit und Abwehrender Brandschutz, Fakultät für Maschinenbau und Sicherheitstechnik, Bergische Universität Wuppertal, Gaußstr. 20, 42119 Wuppertal, Germany

* Correspondence: carsten.jenne@uni-wuppertal.de

Abstract: Homopolyatomic cations of the main group elements and of the element sulfur, in particular, are used as tutorial examples to teach structure and bonding in inorganic chemistry. So far, the cations $[S_4]^{2+}$, $[S_8]^{2+}$, $[S_{19}]^{2+}$, $[S_5]^{\bullet+}$, and $[S_8]^{\bullet+}$ are known experimentally. In this report, the generation and crystal structure determination of the salt $Na_2[S_{20}]_2[B_{12}Cl_{12}]_3$, containing the new homopolyatomic sulfur cation $[S_{20}]^{2+}$, is reported. The structure of the latter cation consists of two seven-membered homocycles, which are bridged by a six-membered sulfur chain. This structure is strongly related to that of $[S_{19}]^{2+}$. The heptasulfur rings show pronounced bond alternation. Comparison with the experimental structures of $[S_7X]^+$ ($X = I, Br$) and the application of quantum chemical calculations show unambiguously that the observed structural features are intrinsic properties of the cationic *cyclo*-heptasulfur moieties. The latter can occupy different conformations, which only slightly differ in energy. Charge delocalization and negative hyperconjugation contribute to the stability of the observed structures. The discovery of the $[S_{20}]^{2+}$ cation fits well into range of known homopolyatomic sulfur cations, which can be classified by their averaged oxidation state of sulfur.

Keywords: crystal structures; *closo*-dodecaborates; *cyclo*-heptasulfur; homopolyatomic cations; non-metal cations; sulfur; weakly coordinating anions



Academic Editors: Axel Klein and Hicham Idriss

Received: 10 December 2024

Revised: 7 January 2025

Accepted: 8 January 2025

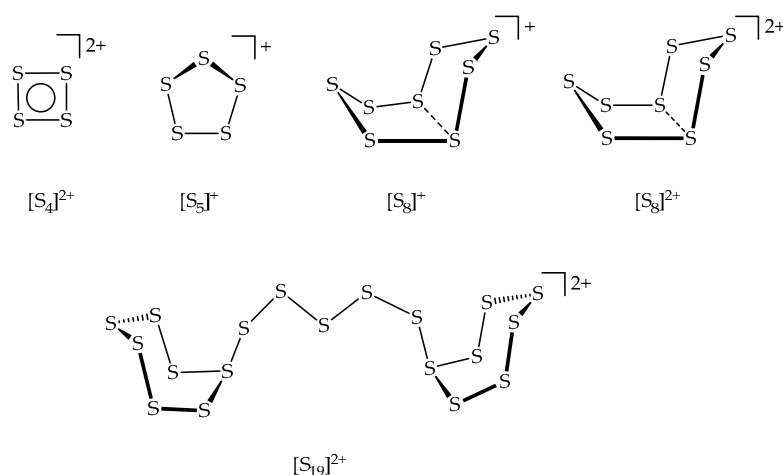
Published: 15 January 2025

Citation: Derendorf, J.; Heiderich, L.; Jenne, C.; Nierstenhöfer, M.C. The Homopolyatomic Sulfur Cation $[S_{20}]^{2+}$. *Inorganics* **2025**, *13*, 23. <https://doi.org/10.3390/inorganics13010023>

Copyright: © 2025 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

1. Introduction

The homopolyatomic cations of the non-metal elements are used as tutorial examples to teach structures and bonding in main group chemistry. They have become important textbook compounds and are reviewed numerous times [1–7]. In particular, homopolyatomic sulfur cations have fascinated chemists for more than 200 years due to their intense colors [8]. In 1804, Buchholz reported an intense blue color upon dissolving sulfur in oleum [9]. Later on, the origin of this blue color was attributed to the presence of different homopolyatomic cations of the element sulfur [10]. To date, three homopolyatomic sulfur dications, $[S_4]^{2+}$ [11–14], $[S_8]^{2+}$ [11,14–16], and $[S_{19}]^{2+}$ [14,17], and the monocationic radical $[S_8]^{\bullet+}$ [18] have been structurally characterized in a solid state. The dication $[S_4]^{2+}$ has a square planar structure. Both eight-membered cations $[S_8]^{2+}$ and $[S_8]^{\bullet+}$ consist of an eight-membered sulfur ring in a chair conformation with a distinct transannular sulfur–sulfur contact. The large dication $[S_{19}]^{2+}$ consists of two seven-membered rings connected by a five-membered sulfur chain. Scheme 1 summarizes the homopolyatomic sulfur cations that were experimentally known prior to this work.



Scheme 1. Structures of the known homopolyatomic sulfur cations.

In the past, homopolyatomic sulfur cations were typically prepared by the oxidation of elemental sulfur using a strong oxidizing agent (e.g., AsF_5 , SbF_5) in superacidic solutions (typical solvents include oleum, HSO_3F , HF , and SO_2) [2]. Following this general procedure, salts containing the dications $[S_4]^{2+}$, $[S_8]^{2+}$, and $[S_{19}]^{2+}$, partnered by fluorinated anions, have been isolated in the solid state [2,6,8].

In contrast, the composition of superacidic solutions of such cations is still not completely understood. Homopolyatomic sulfur compounds cannot be studied by NMR spectroscopy due to the absence of an appropriate NMR nucleus. Based on UV–visible, IR, and, in particular, ESR investigations in solution, the existence of the radicals $[S_{12}]^{\bullet+}$, $[S_8]^{\bullet+}$, $[S_7]^{\bullet+}$, $[S_5]^{\bullet+}$, and $[S_4]^{\bullet+}$ was proposed [15,19,20]. Later on, $[S_5]^{\bullet+}$ was unambiguously identified by ESR experiments using ^{33}S -enriched sulfur [21]. Crossing and Passmore suggested that the presence of $[S_6]^{2+}$ in solution was responsible for the typical blue color of solutions of homopolyatomic cations [10]. Gillespie et al. demonstrated that the composition of the solution is strongly dependent on their acidity level [17]. A blue solution of the composition $[S_8][AsF_6]_2$ takes up additional elemental sulfur up to attain a composition corresponding to $[S_{16}][AsF_6]_2$. At this point, the color changed from blue to red. Gillespie suggested that $[S_{16}]^{2+}$ may exist in equilibrium with $[S_8]^{\bullet+}$ in solution [15]. The determination of the crystal structure of the $[S_{19}]^{2+}$ dication changed his opinion and he discarded the existence of $[S_{16}]^{2+}$ [17]. Recently, we reported the crystal structure of a salt indeed containing the $[S_8]^{\bullet+}$ radical cation [18]. The determination of the crystal structure of $[S_{19}][AsF_6]_2$ [14,17] ($[S_{19}]^{2+}$ can be formulated as $[cyclo-S_7-S_5-cyclo-S_7]^{2+}$) led Passmore et al. to the presumption that other related cations of the type $[cyclo-S_7-S_x-cyclo-S_7]^{2+}$ ($x = 2-6$) might exist as well [22].

In this paper, we report the crystal structure of the new homopolyatomic sulfur dication $[S_{20}]^{2+}$ (which corresponds to $[cyclo-S_7-S_6-cyclo-S_7]^{2+}$), which is strongly related to that of the known $[S_{19}]^{2+}$ cation.

2. Results and Discussion

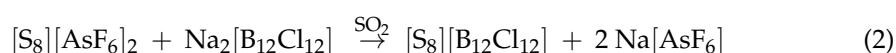
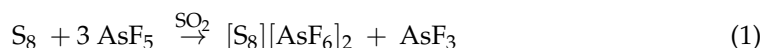
2.1. Generation of $Na_2[S_{20}]_2[B_{12}Cl_{12}]_3$ Single Crystals

All homopolyatomic sulfur cations isolated in the solid state prior to the start of our work ($[S_4]^{2+}$, $[S_8]^{2+}$, $[S_{19}]^{2+}$) were dications and were partnered by fluorometallate counter anions. For many years, the existence of further homopolyatomic sulfur cations was anticipated. However, despite several attempts, other than the three known homopolyatomic sulfur cations could not be isolated in a solid state using the “classical methods”.

In our group, we have been investigating halogenated *closo*-dodecaborates $[B_{12}X_{12}]^{2-}$ ($X = F - I$) as weakly coordinating anions that stabilize reactive cations in the solid state for

more than 15 years [23–31]. This has led us to develop the idea of bringing a new twist to the old topic of homopolyatomic sulfur cations by changing the fluorometallate counter anions into the chlorinated *closo*-dodecaborate $[B_{12}Cl_{12}]^{2-}$.

In classical reactions yielding homopolyatomic sulfur cations, elemental sulfur is oxidized by, for instance, AsF_5 [2]. The $[AsF_6]^-$ counter anions are formed in situ in these reactions (Equation (1)). The chlorinated *closo*-dodecaborate $[B_{12}Cl_{12}]^{2-}$ cannot be introduced the same way. Simple metathesis reactions of the soluble salts $[S_8][AsF_6]_2$ and $Na_2[B_{12}Cl_{12}]$ in liquid sulfur dioxide were unsuccessful because a mixture of the two completely insoluble solids $[S_8][B_{12}Cl_{12}]$ and $Na[AsF_6]$ was obtained (Equation (2)). However, replacing Na^+ by $[NBu_4]^+$ led to the formation of the soluble by-product $[NBu_4][AsF_6]$, which could be removed (Equation (3)).



Unfortunately, the blue solid product, which was assumed to be $[S_8][B_{12}Cl_{12}]$, was completely insoluble in liquid sulfur dioxide and in anhydrous hydrogen fluoride. Typical organic solvents are incompatible with homopolyatomic sulfur cations. For instance, they undergo cycloaddition reactions with nitriles [32,33]. The very low solubility of salts like $[S_8][B_{12}Cl_{12}]$ is caused by their high lattice energy. It should be noted that the lattice energy of a salt of the type $M^{2+}X^{2-}$ is approximately four times higher than that of a salt of the type M^+X^- . The amorphous blue product did not show any pattern in X-ray powder diffraction experiments, did not show a Raman spectrum due to very strong fluorescence, and did not show a decisive IR spectrum. Thus, crystal structure determination was the only way to actually characterize the material. From one crystallization attempt in supercritical sulfur dioxide ($T_c = 158\text{ }^\circ\text{C}$, $p_c = 77.8\text{ atm}$) [34,35], we isolated blue single crystals of the composition $Cs_{0.73}Na_{0.27}[S_8][B_{12}Cl_{12}]$, which we reported previously [18]. Another attempt starting from material with a composition corresponding to $[S_{10}][B_{12}Cl_{12}]$ ($[S_8][B_{12}Cl_{12}]$ + excess S_8) yielded blue crystals of $Na_2[S_{20}]_2[B_{12}Cl_{12}]_3$. The latter contained the previously unknown $[S_{20}]^{2+}$ cation. Its structure will be discussed in the following section.

2.2. Crystal Structure of $Na_2[S_{20}]_2[B_{12}Cl_{12}]_3$

The crystal structure of $Na_2[S_{20}]_2[B_{12}Cl_{12}]_3$ consists of $[B_{12}Cl_{12}]^{2-}$ dianions, sodium cations, and $[S_{20}]^{2+}$ dications (Figure 1). The B–B and B–Cl bond lengths within the $[B_{12}Cl_{12}]^{2-}$ dianion are identical to those of $[B_{12}Cl_{12}]^{2-}$ anions in other crystal structures [30] and are very different to those in neutral $B_{12}Cl_{12}$ [24,31]. Thus, it can be concluded that the $[B_{12}Cl_{12}]^{2-}$ is actually a dianion. The sodium cations originate from the compound $Na_2[B_{12}Cl_{12}]$, which has been used to generate the corresponding salt of the homopolyatomic sulfur cation (for experimental details see Section 3). Their presence seems to be important for crystallization.

The $[S_{20}]^{2+}$ dication (Figure 1) consists of two seven-membered sulfur homocycles (S1–S7 and S14–S20), which are bridged by a six-membered chain (S8–S13). This structure is very similar to that of $[S_{19}]^{2+}$ [14,17], in which the bridging sulfur chain has a length of five atoms, and that of the selenium homopolyatomic cation $[Se_{17}]^{2+}$, in which the seven-membered rings are bridged by three selenium atoms (Figure 2) [36,37].

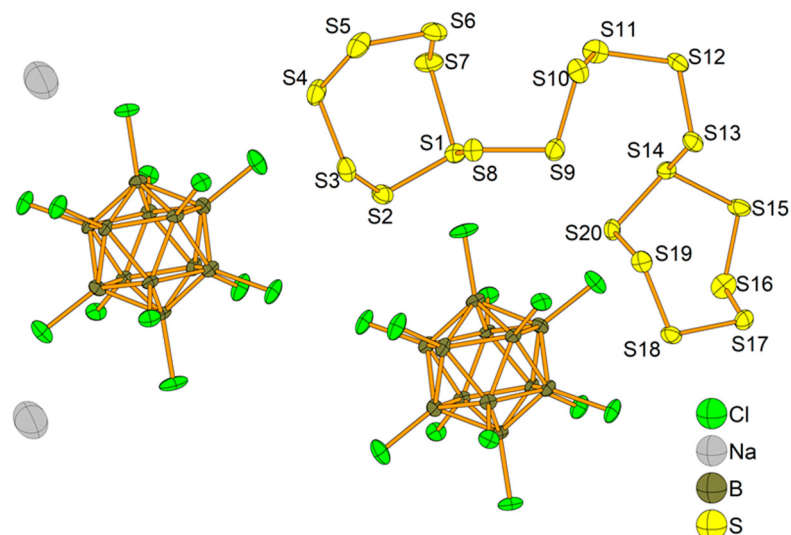


Figure 1. Part of the crystal structure of $\text{Na}_2[\text{S}_{20}]_2[\text{B}_{12}\text{Cl}_{12}]_3$. Ellipsoids are drawn at 50% probability. The $[\text{S}_{20}]^{2+}$ dication is partly disordered and only the major component of the $[\text{S}_{20}]^{2+}$ dication is shown here.

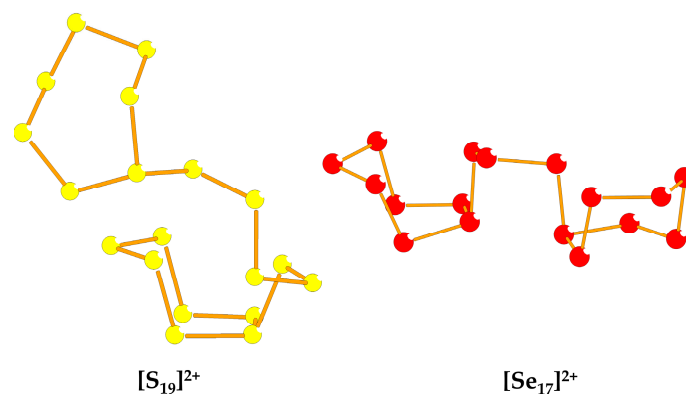


Figure 2. The $[\text{S}_{19}]^{2+}$ (left) and the $[\text{Se}_{17}]^{2+}$ (right) cations in the crystal structures of $[\text{S}_{19}][\text{SbF}_6]_2$ and $[\text{Se}_{17}][\text{NbCl}_6]_2$, respectively, are shown [14,36]. Ellipsoids are drawn with arbitrary radii. All seven-membered homocycles take conformation **B** (see Section 2.3 for further explanation).

The S–S bond lengths within the $[\text{S}_{20}]^{2+}$ cation vary over a very large range from 191 to 239 pm (Table 1) and deviate substantially from the value for a typical S–S single bond (cf. approx. 205 pm in S_8) [38]. The reasons for the observed bond lengths and the preference for the formation of seven-membered rings will be discussed in Section 2.3.2.

Table 1. Selected bond lengths in the $[\text{S}_{20}]^{2+}$ dication. The numbering of the atoms refers to Figure 1^a.

Bond	Bond Length [pm]	Bond	Bond Length [pm]
S1–S2	209.9(2)	S10–S11	204.34(10)
S2–S3	199.7(2)	S11–S12	208.7(2)
S3–S4	212.7(2)	S12–S13	202.9(2)
S4–S5	196.7(2)	S13–S14	210.0(2)
S5–S6	217.6(2)	S14–S15	219.9(3)
S6–S7	191.4(2)	S15–S16	201.0(3)
S1–S7	239.0(2)	S16–S17	207.3(2)
S1–S8	203.8(2)	S17–S18	202.8(3)
S8–S9	204.9(2)	S18–S19	207.3(3)
S9–S10	205.3(2)	S19–S20	202.7(2)

^a Only bond lengths for the major component are given.

While one of the two S7-rings (atoms S1–S7) is perfectly ordered, the second S7-ring (S14–S20) is disordered over two sites (Figure 3). The ratio of the major component (85%, yellow) and the minor component (15%, blue) was freely refined by referring to a single variable.

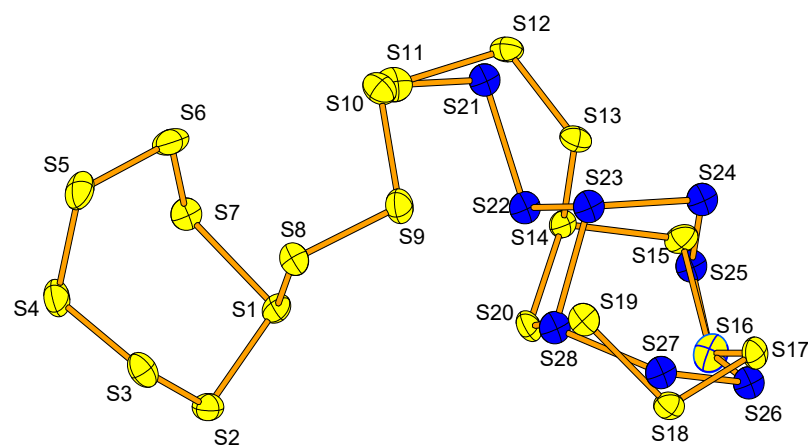


Figure 3. Disorder of the $[S_{20}]^{2+}$ cation in $Na_2[S_{20}]_2[B_{12}Cl_{12}]_3$. Ellipsoids are drawn at 50% probability. Color code: yellow—major component; blue—minor component.

The ordered part of the cation is completely surrounded by $[B_{12}Cl_{12}]^{2-}$ anions and thus forms only S...Cl contacts with neighboring anions. In contrast, the disordered part shows S...Cl contacts with $[B_{12}Cl_{12}]^{2-}$ anions and S...S intermolecular contacts with neighboring $[S_{20}]^{2+}$ cations (Figure 4a). See Figures S2 and S3 in the Supplementary Material for visualizations of the packing in the solid state.

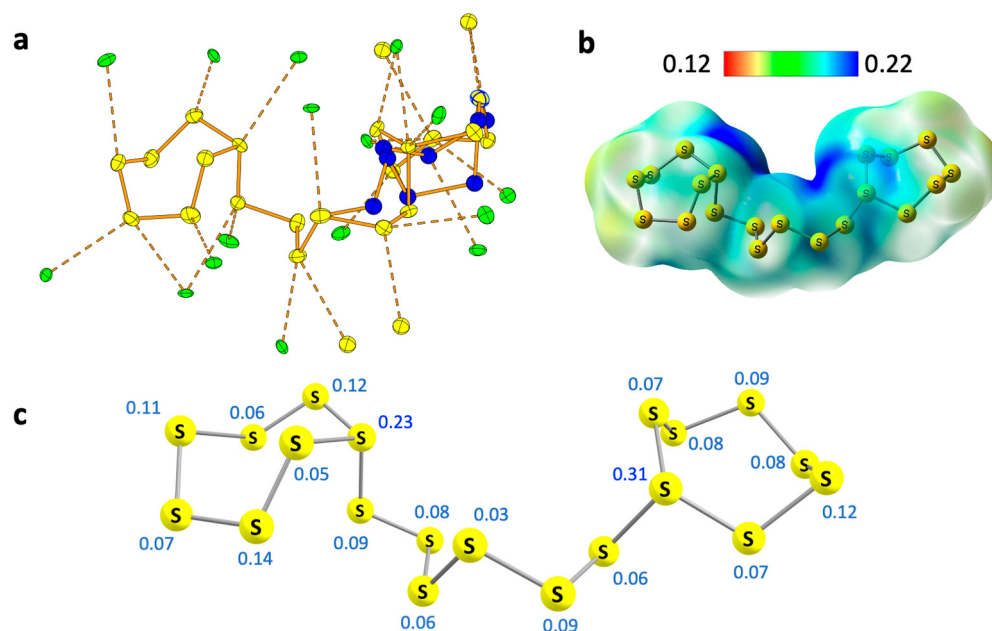


Figure 4. (a) An illustration of the coordination environment around the $[S_{20}]^{2+}$ cation in $Na_2[S_{20}]_2[B_{12}Cl_{12}]_3$. Ellipsoids are drawn at 50% probability. Color code: yellow—major component (sulfur); blue—minor component (sulfur), green—chlorine. Only intermolecular contacts (dotted lines) shorter than the sum of the van der Waals radii (360 pm) [39] are shown. (b) The calculated (GD3BJ + PBE0/def2-TZVPP) molecular electrostatic potential of $[S_{20}]^{2+}$. (c) Calculated (GD3BJ + PBE0/def2-TZVPP) NBO charges.

The positive +2 charge of the cation is delocalized over the entire cation, with a slightly higher positive charge on the bridgehead atoms (Figure 4c). The calculated molecular

electrostatic potential also shows only small deviation from an equal charge distribution (Figure 4b). It appears that the almost uniform charge distribution over the entire cation allows for some fluxional behavior of the corresponding S_7 -rings. Details of the cation structure are discussed in Section 2.3 with the help of quantum chemical calculations.

The structure of the $[S_{20}]^{2+}$ cation is strongly related to the known crystal structures of $[S_{19}]^{2+}$ and $[Se_{17}]^{2+}$ (Figure 2) [14,17,36,37]. Obviously, all three dications consisting of seven-membered rings bridged by a chain of variable length belong to the same class of homopolyatomic chalcogen cations. Figure 5 visualizes the two independent seven-membered sulfur homocycles in the $[S_{20}]^{2+}$ dication. For the disordered ring, only the major component is shown. Both seven-membered rings occupy a chair conformation but, when arranged in the same way (Figure 5), it becomes obvious that the substitution pattern is different. In the ordered part of the molecule (atoms S1–S7), the sulfur chain is attached to atom S1 (conformation A, left in Figure 5), while in the disordered part (atoms S14–S20 for the main component), the sulfur chain is bonded to an atom of the planar four-membered part of the homocycle (conformation B, right in Figure 5).

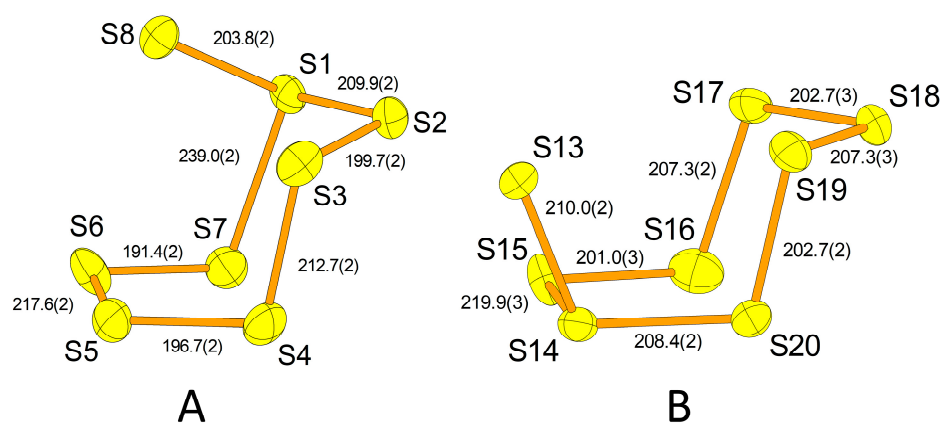


Figure 5. A visualization of the two independent seven-membered sulfur homocycles in the $[S_{20}]^{2+}$ dication in the crystal structure of $Na_2[S_{20}]_2[B_{12}Cl_{12}]_3$. Ellipsoids are drawn at 50% probability.

2.3. Structure and Bonding in $[S_{20}]^{2+}$

The experimental findings raise a number of questions. Is the observed wide variance of the S–S bond lengths (196 to 239 pm) from the length of a typical single bond (205 pm) real? Why are two different conformations (A and B) of the seven-membered homocycles found? Is there a preference for seven-membered over eight-membered cycles?

A quantum chemical geometry optimization of $[S_{20}]^{2+}$, starting from the experimental structure, yields a structure that is in very close agreement with the experimental structure (Figure S5 in the Supplementary Material). This indicates that the experimentally observed bond lengths in $[S_{20}]^{2+}$ indeed are not an artifact of the experimental crystal structure determination. In the following subsections, the structure of $[S_{20}]^{2+}$ and the bonding in $[S_{20}]^{2+}$ will be discussed in detail.

2.3.1. The Preference for Seven-Membered Cycles in $[S_{20}]^{2+}$

The most stable neutral sulfur allotrope is the *cyclo*- S_8 crown. Other sulfur allotropes including *cyclo*-heptasulfur S_7 are known but are much less stable [40,41]. Eight-membered sulfur homocycles are also found in the $[S_8]^{2+}$ dication [11,14–16] and in the open-shell $[S_8]^{\bullet+}$ radical cation [18]. However, when it comes to monocationic closed-shell sulfur homocycles, seven-membered rings seem to be preferred. S_7 homocycles have been experimentally found in the cations $[S_7X]^+$ ($R = Br, I$) [12,13,22] and $[S_{19}]^{2+}$ (*cyclo*- S_7 - S_4 -*cyclo*- S_7) $^{2+}$ [14,17]), as well as in neutral S_7O [42]. Other derivatives of $[S_7X]^+$ ($X = F, Cl, CN, OCN, SCN, SeCN$) have been reported as well, but their crystal structures could not be

determined due to their low thermal stability [43,44]. The most simple derivative $[S_7H]^+$ was shown to have a branched structure with a six-membered ring ($[cyclo-S_6-SH]^+$) by quantum chemical calculations [45]. A similar finding was made for the protonated S_8 molecule, which also prefers a branched $[cyclo-S_7-SH]^+$ structure over the protonated S_8 crown $[HS_8]^+$, although energy differences are small (see Ref [45] and Figure S9 in the Supplementary Material). In contrast, branched structures are much less stable for neutral sulfur homocycles (cf. *cyclo-S₇* vs. *cyclo-S₆-S*) [46]. The open-shell radical cations $[S_7]^+$ and $[S_8]^+$ also prefer non-branched structures [18,47].

Obviously, branched structures with a three-coordinated sulfur atom are energetically preferred, when the molecules are closed-shell and carry a positive charge. The majority of the structurally determined *cyclo*-heptasulfur structures occupy conformation **A**, but conformation **B** has also been reported as well. In the following subsections, we will discuss the structural properties and the bonding situation (Section 2.3.2) of *cyclo*-heptasulfur structures with conformation **A** and address the energy difference between conformations **A** and **B** (Section 2.3.3).

2.3.2. Bonding and Structural Properties in $[S_7R]^+$ Moieties

Table 2 summarizes experimental and calculated S–S bond lengths in compounds with a $[S_7R]^+$ moiety in conformation **A**. It should be noted that the experimentally measured bond lengths and their deviation from a typical S–S single bond (205 pm) [38] were reproduced very well by DFT calculations for all compounds in this study. Therefore, it can be concluded that the observed structural features are real and intrinsic properties of the *cyclo*-heptasulfur homocycles.

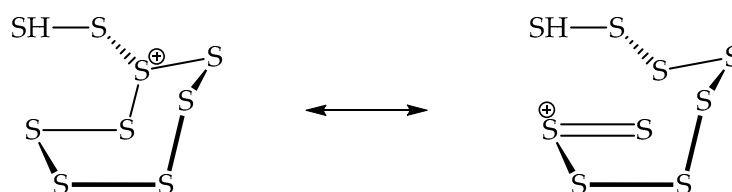
Table 2. Experimental (X-ray) ^a and calculated (GD3BJ + PBE0/def2-TZVPP, in *italics*) S–S bond lengths [pm] of selected compounds containing the $[S_7R]^+$ moiety in conformation **A**.

Compound	S1–S2	S2–S3	S3–S4	S4–S5	S5–S6	S6–S7	S7–S1
$[S_7I][SbF_6]$ [22] ^a	210.4(4) <i>207.4</i>	200.4(4) <i>200.0</i>	211.4(4) <i>210.7</i>	196.3(4) <i>197.2</i>	218.4(4) <i>216.9</i>	190.6(4) <i>190.7</i>	238.9(4) <i>235.2</i>
S_7O [42] ^a	216.3(2) <i>214.8</i>	201.4(2) <i>200.7</i>	212.1(2) <i>209.9</i>	198.7(2) <i>197.6</i>	219.6(2) <i>217.4</i>	195.7(2) <i>194.4</i>	228.3(2) <i>227.4</i>
$[(S_7I)_2I][SbF_6]_3$ [13] ^a	211(1) <i>207.4</i>	200(1) <i>200.0</i>	208(1) <i>210.7</i>	199(2) <i>197.2</i>	221(1) <i>216.9</i>	190(1) <i>190.7</i>	231(1) <i>235.2</i>
$[(S_7I)_4S_4][AsF_6]_6$ [13] ^a	208(1) <i>207.4</i>	199(2) <i>200.0</i>	211(2) <i>210.7</i>	200(2) <i>197.2</i>	219(2) <i>216.9</i>	189(2) <i>190.7</i>	234(1) <i>235.2</i>
$[S_7Br][SbF_6]$ [12] ^a	211(2) <i>206.7</i>	200(2) <i>200.1</i>	211(2) <i>210.7</i>	196(2) <i>197.2</i>	218(2) <i>216.7</i>	193(2) <i>190.5</i>	234(2) <i>235.7</i>
$[S_7Cl][SbF_6]$	N/A <i>206.7</i>	N/A <i>200.3</i>	N/A <i>210.7</i>	N/A <i>197.3</i>	N/A <i>216.6</i>	N/A <i>190.7</i>	N/A <i>235.4</i>
$[S_7F][SbF_6]$	N/A <i>201.8</i>	N/A <i>202.8</i>	N/A <i>209.9</i>	N/A <i>197.4</i>	N/A <i>216.3</i>	N/A <i>192.0</i>	N/A <i>228.7</i>
$[S_7SH][SbF_6]$	N/A <i>208.5</i>	N/A <i>200.0</i>	N/A <i>211.2</i>	N/A <i>197.1</i>	N/A <i>217.2</i>	N/A <i>190.8</i>	N/A <i>235.6</i>
$[S_7SSH][SbF_6]$	N/A <i>207.2</i>	N/A <i>201.2</i>	N/A <i>210.4</i>	N/A <i>197.3</i>	N/A <i>216.8</i>	N/A <i>191.9</i>	N/A <i>231.1</i>
$Na_2[S_{20}]_2[B_{12}Cl_{12}]_3$	209.9(2) <i>207.8</i>	199.7(2) <i>200.8</i>	212.7(2) <i>210.7</i>	196.7(2) <i>197.3</i>	217.6(2) <i>216.5</i>	191.4(2) <i>191.4</i>	239.0(2) <i>234.4</i>

^a The references refer to experimental crystal structure data.

The sulfur–sulfur bonds show a pronounced bond alternation, which is typical for S_7 -rings [12–14,17,22]. The bonds S1–S2, S2–S3, and S3–S4 show the smallest deviation from the length of an S–S single bond. The bonds S4–S5 and S5–S6 are about 10 pm shorter and longer, respectively, than expected. The largest deviations are found for the bonds S6–S7 and S7–S1. The bond S6–S7 (190 pm on average) is almost 15 pm shorter than a typical single bond and belongs to the shortest S–S bonds reported so far [48,49]. In contrast, the bond S7–S1 is extremely long (235–239 pm) and resembles the S–S bond length in dithionite

$[\text{S}_2\text{O}_4]^{2-}$ [50,51], which roughly corresponds to a bond order of 0.5. This situation is easily described by two mesomeric valence bond structures (Scheme 2). DFT calculations give Wiberg bond indices (Figure S8 in the Supplementary Material) of 0.6 for the S7–S1 bond and 1.4 for the S6–S7 bond and thus are in accord with the valence bond structures.



Scheme 2. Mesomeric valence bond structures for $[\text{S}_7\text{X}]^+$ in conformation A ($\text{X} = \text{SSH}$).

In the valence bond structures, the positive formal charge is localized on the three-coordinated sulfur atom S1 [46] and on the atom S6, respectively. To obtain a deeper understanding of structure and bonding, we quantum chemically calculated the structure of the branched $[\text{cyclo-S}_7\text{-SSH}]^+$ cation. The substituent -SSH mimics the chain of sulfur atoms in the structure of $[\text{S}_{20}]^{2+}$ when capped after two sulfur atoms. These DFT calculations reveal the positive charge in $[\text{cyclo-S}_7\text{-SSH}]^+$ to be delocalized over the entire cation, but the highest positive charge is still located on atoms S1 and S6 (see Figures 6a and S7 in the Supplementary Material).

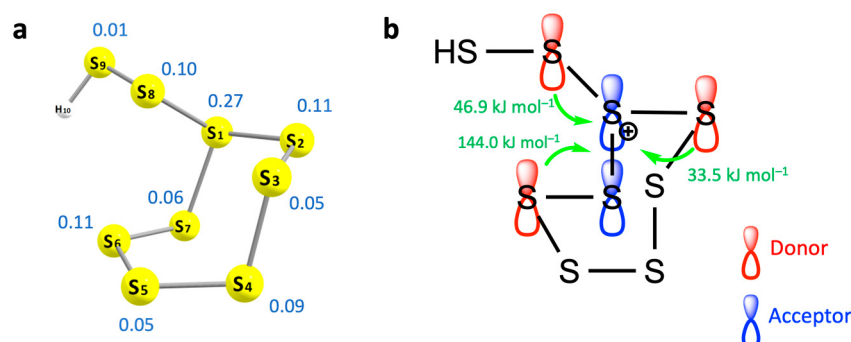


Figure 6. (a) Calculated NBO charges for branched $[\text{cyclo-S}_7\text{-SSH}]^+$ (GD3BJ + PBE0/def2-TZVPP). (b) A schematic representation of important donor–acceptor interactions (negative hyperconjugation) between occupied p orbitals (lone pairs, red) and the adjacent antibonding empty σ^* -orbital of the S1–S7 bond (blue) and calculated NBO stabilization energies (GD3BJ + PBE0/def2-TZVPP).

An NBO [52] analysis was performed in order to identify internal stabilization effects via negative hyperconjugation (Figure 6b and Section S4 in the Supplementary Material) [53,54]. The antibonding σ^* orbital of the S7–S1 bond is coplanar to the p-lone pairs on the sulfur atoms S2, S6, and S8. Therefore, they are all able to donate electron density into the S7–S1 σ^* orbital. This leads to a delocalization of the positive charge, an occupancy of the antibonding S7–S1 σ^* orbital by approximately 0.5 electrons, a shortening of the bonds S1–S2, S6–S7, and S1–S8, an extreme lengthening of the S7–S1 bond up to 231.1 pm, and an overall energetic stabilization of the entire cation. The most important contribution comes from the sulfur atom S6 which reduces its electron density by negative hyperconjugation to reduce repulsive interaction with the coplanar electron pair on the adjacent sulfur atom S5. For neutral *cyclo-S₇* in chair conformation, the importance of negative hyperconjugation has been discussed before [6,46]. Thus, the observed structural features in *cyclo*-heptasulfur cations are the result of intramolecular charge delocalizing and stabilizing donor–acceptor interactions.

2.3.3. The Preference for Conformation A over Conformation B

We calculated the energy difference between conformations **A** and **B** for various $[S_7X]^+$ cations (Figure 7). The calculated energy differences were generally small ($<13 \text{ kJ mol}^{-1}$). For most X , conformation **A** was slightly preferred. **B** was only found to be more stable for $X = F$ and $-\text{SSH}$ conformations. Interestingly, the energetic order of conformations **A** and **B** just switched between the substituents $-\text{SH}$ and $-\text{SSH}$. Indeed, conformation **B** was found experimentally for the selenium derivative $[\text{cyclo-Se}_7\text{-Se}_2\text{Cl}]^+$ [55], for $[\text{Se}_{17}]^{2+}$ [36,37], and for $[\text{S}_{19}]^{2+}$ [14,17].

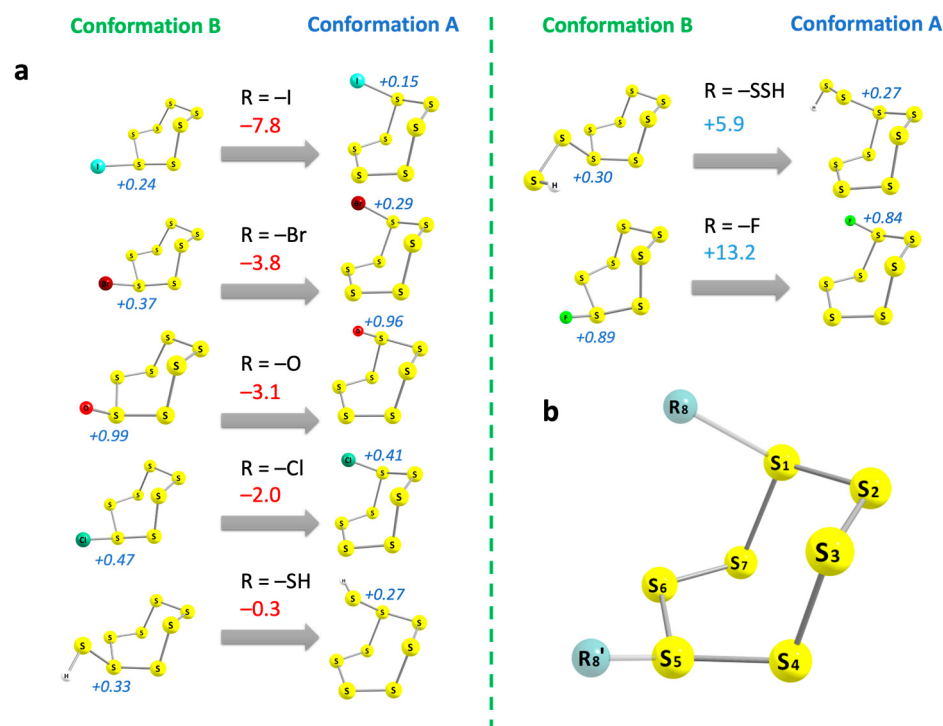


Figure 7. (a) An energetic comparison of different isomers of the cation $[S_7R]^+$ ($R = -I, -Br, -Cl, -SH, -SSH, -F$) and of neutral S_7O at the GD3BJ + PBE0/def2-TZVPP level of theory. Energies are given in kJ mol^{-1} , and NBO charges of the three-coordinated sulfur atoms are shown (*italics*). (b) Numbering scheme of substituted seven-membered rings. R8 corresponds to conformation **A** and R8' represents conformation **B**.

There seems to be no simple correlation explaining the preference for conformation **A** or **B**. In general, the charge delocalization is slightly more pronounced in conformer **A** as evident from the smaller charge on the three-coordinated sulfur atom as compared to conformer **B**. Note that seven-membered chalcogen rings in general are highly fluxional, which was shown by ^{77}Se -NMR spectroscopy in solution [56]. The preference for conformer **A** or **B** is caused by the amount of charge delocalization, negative hyperconjugation, and the repulsion of lone pairs on adjacent sulfur atoms.

Interestingly, the experimental structure of $[\text{S}_{20}]^{2+}$ in the solid state does not exactly resemble the calculated minimum structure in the gas phase. A structure with both rings in conformation **B** was calculated to be lower in energy by 13 kJ mol^{-1} (Figure S5 in the Supplementary Material). In the solid state, crystal packing (Figures S2 and S3 in the Supplementary Material) and cation–anion contacts (Figure 4a) are also important. In addition, the flexibility of the six-membered chain has to be considered, which is determined by the properties of the S–S single bond [57].

To conclude, the small energy differences between different isomers, the high flexibility of the S–S bond, and packing effects in the solid state explain the observed disorder in the crystal structure of $[\text{S}_{20}]^{2+}$.

3. Experimental Section

Experimental details. The starting materials $\text{Na}_2[\text{B}_{12}\text{Cl}_{12}]$ [30] and $[\text{S}_8][\text{AsF}_6]_2$ [11] were prepared by published procedures. Elemental sulfur was purified by sublimation. $[\text{NBu}_4]\text{Br}$ (98%, *FLUKA*, Buchs, Switzerland) was commercially available and used as received. The solvent sulfur dioxide (99.98%, *SCHICK*, Vaihingen/Enz, Germany) was dried over CaH_2 (*MERCK*, Darmstadt, Germany). Reactions using SO_2 were performed in H-shaped glass apparatuses equipped with J. Young valves.

Synthesis of $[\text{NBu}_4]_2[\text{B}_{12}\text{Cl}_{12}]$. $[\text{NBu}_4]\text{Br}$ (2.43 g, 10 mmol) and $\text{Na}_2[\text{B}_{12}\text{Cl}_{12}]$ (3.00 g, 5 mmol) were dissolved in deionized water (8 mL). The product $[\text{NBu}_4]_2[\text{B}_{12}\text{Cl}_{12}]$ precipitated as a white solid, which was separated by filtration and washed with small aliquots of water. After drying in vacuum for one day, the product remained a colorless solid (2.98 g, 3.7 mmol, 74%).

Generation of single crystals of $\text{Na}_2[\text{S}_{20}]_2[\text{B}_{12}\text{Cl}_{12}]_3$. $[\text{NBu}_4]_2[\text{B}_{12}\text{Cl}_{12}]$ and $[\text{S}_8][\text{AsF}_6]$ were dissolved in 1:2 stoichiometry in liquid sulfur dioxide. A dark blue solid precipitated, containing an insoluble blue product and soluble colorless $[\text{NBu}_4][\text{AsF}_6]$. The latter could be removed by repeated washing with liquid sulfur dioxide. The dark blue insoluble residue was expected to be $[\text{S}_8][\text{B}_{12}\text{Cl}_{12}]$ based on the stoichiometry conditions used. The crystallization of this product (5 mg, 1 eq.) and S_8 (2 mg, 1 eq.) in a 10 mm glass ampoule (1 week at 165 °C, cooling rate 1 °C/h) yielded blue single crystals, which were identified as $\text{Na}_2[\text{S}_{20}]_2[\text{B}_{12}\text{Cl}_{12}]_3$.

Crystal structure determination. The single-crystal X-ray structure determination was carried out on a BRUKER (Karlsruhe, Germany) Smart Apex-II CCD system using $\text{Mo-K}\alpha$ (0.71073 Å) radiation. The crystal was mounted onto a cryo loop using fluorinated oil and was frozen in the cold nitrogen stream of the goniometer. The structure was solved by direct methods (*SHELXS*) [58,59] using the crystallography software package *OLEX2* [60]. Subsequent least-squares refinement on F^2 (*SHELXL*) [58,59] located the positions of the remaining atoms in the electron density maps. All atoms were refined anisotropically. The data were corrected for absorption (semi-empirical from equivalents). The crystal structure showed some disorder of the sulfur rings. Ring flipping is common in crystal structures of sulfur rings [17] and relates to the small energy differences between different conformers [61,62]. The ring flipping was modeled as disorder over two sites. Graphical representations of the structure were prepared with the program *DIAMOND 3.2f* [63]. Experimental details for the diffraction experiment are given in Section S2 (Supplementary Material). Crystal data for $\text{B}_{36}\text{Cl}_{36}\text{Na}_2\text{S}_{40}$ ($M = 2993.74$ g/mol) were as follows: triclinic, space group $P\bar{1}$ (no. 2), $a = 9.2556(2)$ Å, $b = 10.7509(3)$ Å, $c = 24.9791(6)$ Å, $\alpha = 80.7800(10)^\circ$, $\beta = 89.0980(10)^\circ$, $\gamma = 86.8860(10)^\circ$, $V = 2449.77(10)$ Å³, $Z = 1$, $T = 100.15(1)$ K, $\mu(\text{MoK}\alpha) = 0.71073$ mm^{−1}, $D_{\text{calc}} = 2.029$ g/cm³, 52,233 reflections measured ($3.844^\circ \leq 2\theta \leq 49.998^\circ$), 8562 unique ($R_{\text{int}} = 0.0386$, $R_{\text{sigma}} = 0.0505$). These values were used in all calculations. The final R_1 was 0.0432 ($I > 2\sigma(I)$) and wR_2 was 0.1150 (all data). Deposition Number 1791488 contains the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service at <https://www.ccdc.cam.ac.uk/structures/> (accessed on 9 January 2025).

Quantum chemical calculations. Geometry optimizing quantum chemical calculations were performed on the GD3BJ + PBE0/def2-TZVPP level of theory. To obtain accurate energies, single-point calculations were performed at CCSD(T)/aug-cc-pVXZ ($X = \text{D, T, Q}$) [64,65] based on the GD3BJ + PBE0/def2-TZVPP geometries and the self-consistent field energies were extrapolated to the complete basis set limit (CBS) using the exponential three-point extrapolation outlined by Halkier et al. for some structures [66]. All basis sets used were implemented in the program package *Gaussian 16, Revision C.02* [67]. We

visualized structures, orbitals, and electro-static potential surfaces using the programs *GaussView 6.0.16* [68] and *Chemcraft 1.8* [69]. NBO analyses were carried out using *NBO 3.1* implemented in *Gaussian 16, Revision C.02* [70].

4. Conclusions

The crystal structure of $\text{Na}_2[\text{S}_{20}]_2[\text{B}_{12}\text{Cl}_{12}]_3$ containing the new homopolyatomic sulfur dication $[\text{S}_{20}]^{2+}$ was determined. The $[\text{S}_{20}]^{2+}$ cation consists of two seven-membered sulfur homocycles and a six-membered bridging sulfur chain ($[\text{cyclo-S}_7\text{-S}_6\text{-cyclo-S}_7]^{2+}$). The structure, although unusual at first sight, is related to those of $[\text{S}_{19}]^{2+}$ and $[\text{S}_7\text{X}]^+$ cations. Comparison and quantum chemical calculations show that the unusual structural features are typical for this type of cation and are the result of charge delocalization and stabilizing intramolecular donor–acceptor interactions (negative hyperconjugation).

The identification of $[\text{S}_{20}]^{2+}$ confirms previous predictions about the existence of previously unknown homopolyatomic sulfur cations and expands the range of known homopolyatomic sulfur cations. Table 3 summarizes all known homopolyatomic sulfur cations.

Table 3. A compilation of experimentally known and quantum chemically predicted homopolyatomic sulfur cations ^a.

Avg. Oxidation State of Sulfur	+1/2	+1/3	+1/4	+1/5	+1/8	+1/9.5	+1/10
Monocation							
Dication	$[\text{S}_4]^{2+}$	$[\text{S}_6]^{2+}$	$[\text{S}_8]^{2+}$	$[\text{S}_5]^+$	$[\text{S}_8]^+$	$[\text{S}_{19}]^{2+}$	$[\text{S}_{20}]^{2+}$
Reference	[11–14]	[10]	[11,14–16]	[21]	[18]	[14,17]	^b

^a Black, bold: experimentally known in the solid state (crystal structure). Green: experimentally known in solution (ESR spectrum). Blue, italics: predicted by quantum chemical calculations. ^b This work.

They can be divided into three different classes depending on the averaged oxidation state of sulfur. The highly oxidized cations $[\text{S}_4]^{2+}$, $[\text{S}_6]^{2+}$, and $[\text{S}_8]^{2+}$ form cyclic dications, whose structures are well understood. At medium oxidation states, cyclic radical cations ($[\text{S}_5]^+$ and $[\text{S}_8]^+$) are formed. The missing cations in between ($[\text{S}_6]^+$ and $[\text{S}_7]^+$) do not exist, because they are unstable with respect to disproportionation [18]. Oxidation states lower than $+1/8$ lead to the formation of dications consisting of two heptasulfur homocycles bridged by a sulfur chain. To date, two examples of the latter class ($[\text{S}_{19}]^{2+}$ and $[\text{S}_{20}]^{2+}$) are known. We expect that $[\text{S}_{17}]^{2+}$ and $[\text{S}_{18}]^{2+}$ might exist as well. It should be noted that the selenium cation $[\text{Se}_{17}]^{2+}$ has been reported [36,37]. However, it could be very difficult to actually isolate $[\text{S}_{17}]^{2+}$ and $[\text{S}_{18}]^{2+}$, because the averaged oxidation state is difficult to adjust experimentally. The choice of the counter ion, which will influence the packing in the solid state, will also play a role. Nevertheless, the story of homopolyatomic sulfur cations might well continue into the future.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/inorganics13010023/s1>, Section S1. Experimental details, Section S2. X-ray diffraction, Section S3. Quantum-chemical calculations, Section S4. NBO Analyses of the A and B Isomer of $[\text{cyclo-S}_7\text{-SSH}]^+$. References [71,72] are cited in the Supplementary Materials.

Author Contributions: Conceptualization, C.J.; methodology, C.J.; investigation, J.D., L.H., C.J. and M.C.N.; writing—original draft preparation, J.D., C.J. and M.C.N.; writing—review and editing, C.J.; funding acquisition, C.J. and M.C.N. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the Deutsche Forschungsgemeinschaft (DFG), grant number JE 714/6-1. M.C.N. was supported by a Kekulé fellowship from the Fonds der Chemischen Industrie.

Data Availability Statement: The original contributions presented in the study are included in the article/Supplementary Material. The optimized coordinates for all quantum chemically calculated

molecules can be accessed and downloaded at <https://doi.org/10.19061/iochem-bd-6-429>. Please note that the data are provided in a specific format, which is compatible with Gaussian, a widely used electronic structure software package. Deposition Number 1791488 contains the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service at <https://www.ccdc.cam.ac.uk/structures/> (accessed on 9 January 2025).

Conflicts of Interest: The authors declare no conflicts of interest.

References

1. Beck, J. Rings, cages and chains—The rich structural chemistry of the polycations of the chalcogens. *Coord. Chem. Rev.* **1997**, *163*, 55–70. [CrossRef]
2. Brownridge, S.; Krossing, I.; Passmore, J.; Jenkins, H.D.B.; Roobottom, H.K. Recent advances in the understanding of the syntheses, structures, bonding and energetics of the homopolyatomic cations of Groups 16 and 17. *Coord. Chem. Rev.* **2000**, *197*, 397–481. [CrossRef]
3. Ahmed, E.; Ruck, M. Homo- and heteroatomic polycations of groups 15 and 16. Recent advances in synthesis and isolation using room temperature ionic liquids. *Coord. Chem. Rev.* **2011**, *255*, 2892–2903. [CrossRef]
4. Engesser, T.A.; Lichtenthaler, M.R.; Schleep, M.; Krossing, I. Reactive p-block cations stabilized by weakly coordinating anions. *Chem. Soc. Rev.* **2016**, *45*, 789–899. [CrossRef] [PubMed]
5. Krossing, I. Homoatomic Cages and Clusters of the Heavier Group 15 Elements: Neutral Species and Cations. In *Molecular Clusters of the Main Group Elements*; Wiley-VCH: Weinheim/Bergstraße, Germany, 2004; pp. 209–229.
6. Krossing, I. Structure and Bonding of the Neutral Chalcogens and their Polyatomic Cations. In *Handbook of Chalcogen Chemistry*; Royal Society of Chemistry: London, UK, 2007; pp. 381–416.
7. Laitinen, R.S.; Oilunkaniemi, R.; McGeachie, L.; Kelly, P.F.; King, R.S.P. Polychalcogen molecules, ligands, and ions Part 1: Homo- and heteronuclear chalcogen rings. In *Comprehensive Inorganic Chemistry III*, 3rd ed.; Elsevier: Oxford, UK, 2023; pp. 934–969.
8. Krossing, I. Homoatomic Sulfur Cations. In *Elemental Sulfur and Sulfur-Rich Compounds I*; Topics in Current Chemistry; Springer: Berlin/Heidelberg, Germany, 2003; Volume 230, pp. 79–92.
9. Bucholz, C.F. Versuche über die Auflösung des Indigs in der Schwefelsäure, als Beytrag zur Ausmittlung des Vorgangs bey derselben. *Neues Allg. J. Der Chem.* **1804**, *3*, 3–29.
10. Krossing, I.; Passmore, J. Evidence for the Blue 10π S_6^{2+} Dication in Solutions of $S_8(AsF_6)_2$: A Computational Study Including Solvation Energies. *Inorg. Chem.* **2004**, *43*, 1000–1011. [CrossRef]
11. Cameron, T.S.; Deeth, R.J.; Dionne, I.; Du, H.; Jenkins, H.D.B.; Krossing, I.; Passmore, J.; Roobottom, H.K. Bonding, Structure, and Energetics of Gaseous E_8^{2+} and of Solid $E_8(AsF_6)_2$ ($E = S, Se$). *Inorg. Chem.* **2000**, *39*, 5614–5631. [CrossRef]
12. Passmore, J.; Sutherland, G.; Whidden, T.K.; White, P.S.; Wong, C.-M. The preparation of S_7BrMF_6 ($M = As, Sb$), and the preparation and crystal structure of $(S_7Br)_4S_4(AsF_6)_6$ containing the bromo-cycloheptasulphur (1+) cation. *Can. J. Chem.* **1985**, *63*, 1209–1214. [CrossRef]
13. Passmore, J.; Sutherland, G.; White, P.S. Preparation and X-ray Crystal Structure of *m*-Iodo-bis(4-iodo-cyclo-heptasulfur) Tris(hexafluoroantimonate)-Bis(arsenic trifluoride), $[(S_7I)_2I](SbF_6)_3 \cdot 2AsF_3$, and $(S_7I)_4S_4(AsF_6)_6$ Containing the Iodo-cyclo-heptasulfur(1+) and the Tetrasulfur(2+) Cations. *Inorg. Chem.* **1982**, *21*, 2717–2723. [CrossRef]
14. Faggiani, R.; Gillespie, R.J.; Sawyer, J.F.; Vekris, J.E. Structures of nonadecasulfur(2+) bis[hexafluoroantimonate(1-)] $S_{19}(SbF_6)_2$, octasulfur(2+) di- μ -fluoro-dodecafluorotriantimonate(1-) hexafluoroantimonate(1-) $S_8(Sb_3F_{14})(SbF_6)$, and tetrasulfur(2+) di- μ -fluoro-difluorodiantimony(2+) μ -fluoro-tetrafluorodiantimony(1+) pentakis[hexafluoroantimonate(1-)] $S_4(Sb_2F_4)(Sb_2F_5)(SbF_6)_5$. *Acta Crystallogr. Sect. C Cryst. Struct. Commun.* **1989**, *45*, 1847–1853.
15. Gillespie, R.J.; Passmore, J.; Ummat, P.K.; Vaidya, O.C. Polyatomic cations of sulfur. I. Preparation and properties of S_{16}^{2+} , S_8^{2+} , and S_4^{2+} . *Inorg. Chem.* **1971**, *10*, 1327–1332. [CrossRef]
16. Davies, C.G.; Gillespie, R.J.; Park, J.J.; Passmore, J. Polyatomic cations of sulfur. II. Crystal structure of octasulfur bis(hexafluoroarsenate), $S_8(AsF_6)_2$. *Inorg. Chem.* **1971**, *10*, 2781–2784. [CrossRef]
17. Burns, R.C.; Gillespie, R.J.; Sawyer, J.F. Preparation and crystal structure of nonadecasulfur bis(hexafluoroarsenate) and an ESR and absorption spectral study of solutions containing the nonadecasulfur(2+) cation and related systems. *Inorg. Chem.* **1980**, *19*, 1423–1432. [CrossRef]
18. Derendorf, J.; Jenne, C.; Keßler, M. The First Step of the Oxidation of Elemental Sulfur: Crystal Structure of the Homopolyatomic Sulfur Radical Cation $[S_8]^+$. *Angew. Chem. Int. Ed.* **2017**, *56*, 8281–8284. [CrossRef] [PubMed]
19. Fehrmann, R.; Bjerrum, N.J.; Pedersen, E. Lower oxidation states of sulfur. 2. Spectrophotometric, potentiometric and ESR study of the sulfur-chlorine system in molten sodium chloride-aluminum chloride (37:63 mol %) at 150 °C. *Inorg. Chem.* **1982**, *21*, 1497–1504. [CrossRef]

20. Symons, M.C.R.; Wilkinson, J.G. Nature of the Paramagnetic Cation in Solutions of Sulphur in Oleum. *Nat. Phys. Sci.* **1972**, *236*, 126–127. [\[CrossRef\]](#)
21. Low, H.S.; Beaudet, R.A. The identification of S_5^+ as a paramagnetic species in sulfur-oleum solutions by electron spin resonance. *J. Am. Chem. Soc.* **1976**, *98*, 3849–3852. [\[CrossRef\]](#)
22. Passmore, J.; Sutherland, G.; Taylor, P.; Whidden, T.K.; White, P.S. Preparations and X-ray crystal structures of iodo-cycloheptasulfur hexafluoroantimonate(V) and hexafluoroarsenate(V), S_7ISbF_6 and S_7IASF_6 . *Inorg. Chem.* **1981**, *20*, 3839–3845. [\[CrossRef\]](#)
23. Knapp, C. Weakly Coordinating Anions: Halogenated Borates and Dodecaborates. In *Comprehensive Inorganic Chemistry II*; Reedijk, J., Poeppelmeier, K., Eds.; Elsevier: Amsterdam, The Netherlands, 2013; Volume 1, pp. 651–679.
24. Boéré, R.T.; Kacprzak, S.; Keßler, M.; Knapp, C.; Riebau, R.; Riedel, S.; Roemmele, T.L.; Rühle, M.; Scherer, H.; Weber, S. Oxidation of $closo-[B_{12}Cl_{12}]^{2-}$ to the Radical Anion $[B_{12}Cl_{12}]^{\cdot -}$ and to Neutral $B_{12}Cl_{12}$. *Angew. Chem. Int. Ed.* **2011**, *50*, 549–552. [\[CrossRef\]](#)
25. Kessler, M.; Knapp, C.; Zogaj, A. Cationic Dialkyl Metal Compounds of Group 13 Elements (E = Al, Ga, In) Stabilized by the Weakly Coordinating Dianion $[B_{12}Cl_{12}]^{2-}$. *Organometallics* **2011**, *30*, 3786–3792. [\[CrossRef\]](#)
26. Bolli, C.; Derendorf, J.; Keßler, M.; Knapp, C.; Scherer, H.; Schulz, C.; Warneke, J. Synthesis, Crystal Structure, and Reactivity of the Strong Methylating Agent $Me_2B_{12}Cl_{12}$. *Angew. Chem. Int. Ed.* **2010**, *49*, 3536–3538. [\[CrossRef\]](#) [\[PubMed\]](#)
27. Derendorf, J.; Keßler, M.; Knapp, C.; Rühle, M.; Schulz, C. Alkali metal-sulfur dioxide complexes stabilized by halogenated *closo*-dodecaborate anions. *Dalton Trans.* **2010**, *39*, 8671–8678. [\[CrossRef\]](#) [\[PubMed\]](#)
28. Kessler, M.; Knapp, C.; Sagawe, V.; Scherer, H.; Uzun, R. Synthesis, Characterization, and Crystal Structures of Silylium Compounds of the Weakly Coordinating Dianion $[B_{12}Cl_{12}]^{2-}$. *Inorg. Chem.* **2010**, *49*, 5223–5230. [\[CrossRef\]](#)
29. Knapp, C.; Schulz, C. How to overcome Coulomb explosions in labile dications by using the $[B_{12}Cl_{12}]^{2-}$ dianion. *Chem. Commun.* **2009**, 4991–4993. [\[CrossRef\]](#) [\[PubMed\]](#)
30. Geis, V.; Gutsche, K.; Knapp, C.; Scherer, H.; Uzun, R. Synthesis and characterization of synthetically useful salts of the weakly-coordinating dianion $[B_{12}Cl_{12}]^{2-}$. *Dalton Trans.* **2009**, 2687–2694. [\[CrossRef\]](#) [\[PubMed\]](#)
31. Boéré, R.T.; Derendorf, J.; Jenne, C.; Kacprzak, S.; Keßler, M.; Riebau, R.; Riedel, S.; Roemmele, T.L.; Rühle, M.; Scherer, H.; et al. On the Oxidation of the Three-Dimensional Aromatics $[B_{12}X_{12}]^{2-}$ (X = F, Cl, Br, I). *Chem. Eur. J.* **2014**, *20*, 4447–4459. [\[CrossRef\]](#) [\[PubMed\]](#)
32. Cameron, T.S.; Decken, A.; Fang, M.; Passmore, J.; Wood, D.J.; Parsons, S. Oxidation of methyl groups in the reaction of sulfur homopolyatomic cations with acetonitrile: Formation and crystal structure of the novel trithietanylium ring. *Chem. Commun.* **1999**, 1801–1802. [\[CrossRef\]](#)
33. Shuvaev, K.V.; Passmore, J. RCN SSS^+ : A novel class of stable sulfur rich radical cations. *Coord. Chem. Rev.* **2013**, *257*, 1067–1091. [\[CrossRef\]](#)
34. Breiting, D.K.; Bogner, A.; Lauter, M.; Loos, R. Supercritical SO_2 for preparation of sulfur dioxide complexes and for recovery of precious metals from used catalysts. In *Supercritical Fluids as Solvents and Reaction Media*; Elsevier: Amsterdam, The Netherlands, 2004; pp. 523–530.
35. Cabrera, C.R.; Garcia, E.; Bard, A.J. Electrochemistry in near-critical and supercritical fluids. *J. Electroanal. Chem. Interfacial Electrochem.* **1989**, *260*, 457–460. [\[CrossRef\]](#)
36. Beck, J.; Fischer, A. $Se_{17}[NbCl_6]_2$ und $Se_{17}[TaBr_6]_2$ —Zwei neue Vertreter des Strukturtyps $Se_{17}[MX_6]_2$. *Z. Anorg. Allg. Chem.* **1997**, *623*, 780–784. [\[CrossRef\]](#)
37. Beck, J.; Wetterau, J. Chalcogen Polycations by Oxidation of Elemental Chalcogens with Transition Metal Halides: Synthesis and Crystal Structure of $[Se_{17}][WCl_6]_2$. *Inorg. Chem.* **1995**, *34*, 6202–6204. [\[CrossRef\]](#)
38. Steudel, R. Homocyclic sulfur molecules. In *Inorganic Ring Systems*; Springer: Berlin/Heidelberg, Germany, 1982; Volume 102, pp. 149–176.
39. Batsanov, S.S. Van der Waals Radii of Elements. *Inorg. Mater.* **2001**, *37*, 871–885. [\[CrossRef\]](#)
40. Steudel, R.; Eckert, B. Solid Sulfur Allotropes. In *Elemental Sulfur and Sulfur-Rich Compounds I*; Topics in Current Chemistry; Springer: Berlin/Heidelberg, Germany, 2003; Volume 230, pp. 1–79.
41. Steudel, R.; Reinhardt, R.; Schuster, F. Crystal and Molecular Structure of *cyclo*-Heptasulfur (δ - S_7). *Angew. Chem. Int. Ed. Engl.* **1977**, *16*, 715. [\[CrossRef\]](#)
42. Steudel, R.; Reinhardt, R.; Sandow, T. Bond Interaction in Sulfur Rings: Crystal and Molecular Structure of *cyclo*-Heptasulfur Oxide, S_7O . *Angew. Chem. Int. Ed. Engl.* **1977**, *16*, 716. [\[CrossRef\]](#)
43. Minkwitz, R.; Nowicki, J. Preparation of Pseudohalidoheptasulfur(+1) Hexafluorometallates $S_7X^+MF_6^-$ (X = CN, OCN, SeCN; M = As, Sb). *Z. Anorg. Allg. Chem.* **1992**, *607*, 96–100. [\[CrossRef\]](#)
44. Minkwitz, R.; Nowicki, J. Chemistry of sulfur halides. 36. Preparation of $S_7X^+MF_6^-$ (X = F, Cl; M = As, Sb) and vibrational spectra of the series S_7X^+ (X = F, Cl, Br, I). *Inorg. Chem.* **1990**, *29*, 2361–2364. [\[CrossRef\]](#)
45. Wong, M.W.; Chwee, T.S.; Steudel, R. Electrophilic Attack on Sulfur–Sulfur Bonds. 1. Protonation of Various Isomers of the Homoatomic Sulfur Molecules S_n ($n = 2–8$). *J. Phys. Chem. A* **2004**, *108*, 7091–7098. [\[CrossRef\]](#)

46. Wong, M.W.; Steudel, Y.; Steudel, R. Isomers of *cyclo*-Heptasulfur and Their Coordination to Li⁺: an Ab Initio Molecular Orbital Study. *Inorg. Chem.* **2005**, *44*, 8908–8915. [CrossRef]
47. Jenne, C.; Nierstenhöfer, M.C. Homopolyatomic Chalcogen Radical Cations of Selenium and Tellurium. *Eur. J. Inorg. Chem.* **2020**, *2020*, 200–207. [CrossRef]
48. Brownridge, S.; Crawford, M.J.; Du, H.B.; Harcourt, R.D.; Knapp, C.; Laitinen, R.S.; Passmore, J.; Rautiainen, J.M.; Suontamo, R.J.; Valkonen, J. Accounting for the differences in the structures and relative energies of the highly homoatomic $np\pi\text{--}np\pi$ ($n \geq 3$)-bonded S₂I₄²⁺, the Se-I π -bonded Se₂I₄²⁺, and their higher-energy isomers by AIM, MO, NBO, and VB methodologies. *Inorg. Chem.* **2007**, *46*, 681–699. [CrossRef]
49. Brownridge, S.; Cameron, T.S.; Du, H.B.; Knapp, C.; Köppe, R.; Passmore, J.; Rautiainen, J.M.; Schnöckel, H. The highest bond order between heavier main-group elements in an isolated compound? Energetics and vibrational spectroscopy of S₂I₄(MF₆)₂ (M = As, Sb). *Inorg. Chem.* **2005**, *44*, 1660–1671. [CrossRef] [PubMed]
50. Dunitz, J. The structure of sodium dithionite and the nature of the dithionite ion. *Acta Crystallogr.* **1956**, *9*, 579–586. [CrossRef]
51. Kajiwar, Y.; Miyata, S.; Nakai, H. Unusual motion of the *n*-methoxypropyl moiety observed in the photochromic crystals of an organorhodium dithionite complex with *n*-methoxypropyltetramethylcyclopentadienyl ligands. *Dalton Trans.* **2022**, *51*, 48–52. [CrossRef]
52. Reed, A.E.; Curtiss, L.A.; Weinhold, F. Intermolecular interactions from a natural bond orbital, donor-acceptor viewpoint. *Chem. Rev.* **1988**, *88*, 899–926. [CrossRef]
53. Alabugin, I.V.; Kuhn, L.; Krivoshchapov, N.V.; Mehaffy, P.; Medvedev, M.G. Anomeric effect, hyperconjugation and electrostatics: Lessons from complexity in a classic stereoelectronic phenomenon. *Chem. Soc. Rev.* **2021**, *50*, 10212–10252. [CrossRef]
54. von Ragué Schleyer, P.; Kos, A.J. The importance of negative (anionic) hyperconjugation. *Tetrahedron* **1983**, *39*, 1141–1150. [CrossRef]
55. Faggiani, R.; Gillespie, R.J.; Kolis, J.W.; Malhotra, K.C. Preparation and X-ray structure of (Se₉Cl)(SbCl₆): A seven-membered selenium ring. *J. Chem. Soc. Chem. Commun.* **1987**, *255*, 591–592. [CrossRef]
56. Steudel, R.; Papavassiliou, M.; Jensen, D.; Seppelt, K. Spectroscopic Evidence for Pseudorotation of Seven-Membered Chalcogen Rings in Solution. *Z. Naturforsch. B Chem. Sci.* **1988**, *43*, 245–248. [CrossRef]
57. Steudel, R. Properties of Sulfur-Sulfur Bonds. *Angew. Chem. Int. Ed. Engl.* **1975**, *14*, 655–664. [CrossRef]
58. Sheldrick, G.M. Crystal structure refinement with SHELXL. *Acta Crystallogr. Sect. C Cryst. Struct. Commun.* **2015**, *71*, 3–8. [CrossRef] [PubMed]
59. Sheldrick, G.M. A short history of SHELX. *Acta Crystallogr. Sect. A Found. Crystallogr.* **2008**, *64*, 112–122. [CrossRef]
60. Dolomanov, O.V.; Bourhis, L.J.; Gildea, R.J.; Howard, J.A.K.; Puschmann, H. OLEX2: A complete structure solution, refinement and analysis program. *J. Appl. Crystallogr.* **2009**, *42*, 339–341. [CrossRef]
61. Cioslowski, J.; Szarecka, A.; Moncrieff, D. Conformations and thermodynamic properties of sulphur homocycles. II. The fluxional S₈⁺ radical cation. *Mol. Phys.* **2002**, *100*, 1559–1566. [CrossRef]
62. Cioslowski, J.; Szarecka, A.; Moncrieff, D. Conformations and Thermodynamic Properties of Sulfur Homocycles. 1. The S₅, S₆, S₇, and S₈ Molecules. *J. Phys. Chem. A* **2001**, *105*, 501–505. [CrossRef]
63. Brandenburg, K. *Diamond v.3.2f*; Crystal Impact GbR: Bonn, Germany, 2001.
64. Woon, D.E.; Dunning, T.H., Jr. Gaussian basis sets for use in correlated molecular calculations. III. The atoms aluminum through argon. *J. Chem. Phys.* **1993**, *98*, 1358–1371. [CrossRef]
65. Kendall, R.A.; Dunning, T.H., Jr.; Harrison, R.J. Electron affinities of the first-row atoms revisited. Systematic basis sets and wave functions. *J. Chem. Phys.* **1992**, *96*, 6796–6806. [CrossRef]
66. Halkier, A.; Helgaker, T.; Jørgensen, P.; Klopper, W.; Olsen, J. Basis-set convergence of the energy in molecular Hartree–Fock calculations. *Chem. Phys. Lett.* **1999**, *302*, 437–446. [CrossRef]
67. Frisch, M.J.; Trucks, G.W.; Schlegel, H.B.; Scuseria, G.E.; Robb, M.A.; Cheeseman, J.R.; Scalmani, G.; Barone, V.; Petersson, G.A.; Nakatsuji, H.L.; et al. *Gaussian 16 Rev. C.02*; Gaussian, Inc.: Wallingford, CT, USA, 2016.
68. Dennington, R.; Keith, T.A.; Millam, J.M. *GaussView, 6.0.16*; Semichem. Inc.: Shawnee Mission, KS, USA, 2016.
69. Chemcraft—Graphical Software for Visualization of Quantum Chemistry Computations. Available online: <https://www.chemcraftprog.com> (accessed on 9 January 2025).
70. Glendening, E.D.; Reed, A.E.; Carpenter, J.E.; Weinhold, F. *NBO Version 3.1*; Gaussian Inc.: Pittsburgh, PA, USA, 2001.

71. Cameron, T.S.; Dionne, I.; Jenkins, H.D.B.; Parsons, S.; Passmore, J.; Roobottom, H.K. Preparation, X-ray Crystal Structure Determination, Lattice Potential Energy, and Energetics of Formation of the Salt $S_4(AsF_6)_2 \cdot AsF_3$ Containing the Lattice-Stabilized Tetrasulfur [2+] Cation. Implications for the Understanding of the Stability of M_4^{2+} and M_2^+ (M = S, Se, and Te) Crystalline Salts. *Inorg. Chem.* **2000**, *39*, 2042–2052.
72. Tiritiris, I.; Schleid, T. Die Kristallstrukturen der Dicaesium-Dodekahalogeno-*closo*-Dodekaborate $Cs_2[B_{12}X_{12}]$ (X = Cl, Br, I) und ihrer Hydrate. *Z. Anorg. Allg. Chem.* **2004**, *630*, 1555–1563. [[CrossRef](#)]

Disclaimer/Publisher’s Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.