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Sulfur

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The First Step of the Oxidation of Elemental Sulfur: Crystal Structure of the Homopolyatomic Sulfur Radical Cation $[S_8]^{\cdot+}$

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Dedicated to Professor Jack Passmore

Abstract: *The oxidation of elemental sulfur in superacidic solutions and melts is one of the oldest topics in inorganic main group chemistry. Thus far, only three homopolyatomic sulfur cations ($[S_4]^{2+}$, $[S_8]^{2+}$, and $[S_{19}]^{2+}$) have been characterized crystallographically although ESR investigations have given evidence for the presence of at least two additional homopolyatomic sulfur radical cations in solution. Herein, the crystal structure of the hitherto unknown homopolyatomic sulfur radical cation $[S_8]^{\cdot+}$ is presented. The radical cation $[S_8]^{\cdot+}$ represents the first step of the oxidation of the S_8 molecule present in elemental sulfur. It has a structure similar to the known structure of $[S_8]^{2+}$, but the transannular sulfur⋯sulfur contact is significantly elongated. Quantum-chemical calculations help in understanding its structure and support its presence in solution as a stable compound. The existence of $[S_8]^{\cdot+}$ is also in accord with previous ESR investigations.*

Homopolyatomic cations of the main group elements have been one of the main themes in p-block chemistry in the second half of the last century. These often very simple compounds with unusual structures forced the development of new models in chemical bonding.[1] Lately, the synthetic strategies and methods that were very successful in the past did not allow for further progress. Nevertheless, by using new methods and techniques, spectacular results were still obtained even recently. For instance, evidence for the first homopolyatomic phosphorus cation $[P_9]^+$ was obtained by using modern weakly coordinating anions instead of classical hexafluorometallates such as $[AsF_6]^-$.[2] The first homopolyatomic antimony cation $[Sb_8]^{2+}$ was stabilized even by the simple chloro anion $[GaCl_4]^-$.[3] Recently, ionic liquids as reaction media[4] and electrochemical syntheses[5] were introduced as new strategies for the field of homopolyatomic cations of the heavier chalcogen elements.

The first generation of a homopolyatomic cation of the main group element sulfur was reported already in 1804, when Buchholz observed an intense blue color upon dissolving elemental sulfur in oleum.[6] The quest for the origin of this intense color and that of similar solutions of other p-block elements in oleum was one of the driving forces for investigations of such systems in superacidic media.[7] A large number of homopolyatomic cations of sulfur and the other p-block elements were discovered and structurally characterized in the solid state, and have been reviewed numerous times.[1,4b,8] Especially the impressive work by Gillespie, Passmore, and co-workers led to the discovery of the three presently known and crystallographically characterized homopolyatomic sulfur cations $[S_4]^{2+}$,[9] $[S_8]^{2+}$,[9a,d,10] and $[S_{19}]^{2+}$.[9d,11] All known structurally characterized homopolyatomic sulfur cations are dications and were crystallized with $[AsF_6]^-$ or $[SbF_6]^-$ counteranions.

In superacidic solutions, the situation is much more complicated. As early as 1957, Symons and Ingram reported evidence for the presence of paramagnetic compounds in the blue solutions of sulfur in oleum.[12] In the 1970s, Gillespie and co-workers thoroughly investigated sulfur cations in superacidic solutions (e.g., oleum, HSO_3F).[10a,11,13] In contrast to other main group elements such as phosphorus[2b,14] and selenium,[15] studies of sulfur and its cations are severely hindered by the absence of a useful nucleus for NMR spectroscopic investigations. Therefore, the characterization is limited to the interpretation of UV/Vis, IR, and electron spin resonance (ESR) spectra of mixtures in solution or the determination of crystal structures from isolated solids. The oxidation of sulfur in liquid sulfur dioxide or superacidic media with strong oxidizing agents gives colored solutions. ESR spectra of these solutions show three different ESR signals, namely a minor signal at $g = 2.008$ and two main signals at $g = 2.027$ and 2.014, which change in intensity during the addition of AsF_5.[11] These signals obviously originate from different sulfur radical cations in different oxidation states, and these sulfur radicals have been discussed controversially. The sulfur radicals $[S_{12}]^{\cdot+}$, $[S_8]^{\cdot+}$, $[S_7]^{\cdot+}$, $[S_5]^{\cdot+}$, and $[S_4]^{\cdot+}$ were suggested to be the origin of these resonances.[10a,11,13,16] Eventually, the ESR signal at $g = 2.014$, which appears at high concentrations of an added oxidizing agent, was unambiguously assigned to $[S_5]^{\cdot+}$ by ESR experiments using ^{33}S-enriched sulfur.[17] Further evidence for the presence of additional currently unidentified sulfur cations comes from the color of these superacidic solutions. Typically, solutions of sulfur in a superacidic medium containing a large excess of an oxidizing agent are blue. However, Gillespie and co-workers discovered that solutions with a formal composition of $[S_{16}][AsF_6]_2$ are red and turn blue only after addition of more oxidizing agent.[11,13] Conversely, a blue solution of $[S_8][AsF_6]_2$ takes up sulfur up to an approximate composition

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of $[S_{19}][AsF_6]_2$, and undergoes a color change from blue to red when an approximate composition of $[S_{16}][AsF_6]_2$ is reached.[18] It was suggested that $[S_{16}]^{2+}$ may exist in equilibrium with $[S_8]^{\bullet +}$ in solution.[10a] However, having determined the crystal structure of $[S_{19}]^{2+}$, Gillespie rejected the existence of $[S_{16}]^{2+}$.[11]

Our previous success in the use of the weakly coordinating anion $[B_{12}Cl_{12}]^{2-}$ for the stabilization of highly reactive cations in the solid state prompted us to pursue a similar approach to investigate homopolyatomic cations of sulfur.[19] First attempts to perform simple metathesis reactions of the soluble salts $[S_8][AsF_6]_2$ and $Na_2[B_{12}Cl_{12}]$ in liquid sulfur dioxide were disappointing because a mixture of the two insoluble solids $[S_8][B_{12}Cl_{12}]$ and $Na[AsF_6]$ was obtained. Replacing Na^+ by $[NBu_4]^+$ led to the formation of the soluble byproduct $[NBu_4][AsF_6]$, which could be removed. However, the remaining blue residue was still insoluble in liquid sulfur dioxide and anhydrous hydrogen fluoride. The insoluble material resisted all attempts to characterize it. The very low solubility is due the high lattice energy of this salt, which consists of a dication and a dianion. In addition, sulfur cations are incompatible with many organic solvents, for instance, they undergo cycloaddition reactions with nitriles;[20] therefore, we decided to use supercritical sulfur dioxide ($T_c = 158\,°C$, $p_c = 77.8$ atm) as a medium for crystallization.[21] Numerous attempts were made to obtain crystalline material in supercritical sulfur dioxide starting from $[S_8][B_{12}Cl_{12}]$, $[S_4][B_{12}Cl_{12}]$, or mixtures of both compounds as well as mixtures of one of the salts with elemental sulfur (see the Supporting Information, Section S1). Eventually, a crystallization attempt with a mixture of equimolar amounts of $[S_8][B_{12}Cl_{12}]$ and $[S_4][B_{12}Cl_{12}]$ gave blue single crystals of the composition $Cs_{0.73}Na_{0.27}[S_8][B_{12}Cl_{12}]$.[22] The structure contains an eight-membered sulfur homocycle aside from alkali metal cations and $[B_{12}Cl_{12}]^{2-}$ dianions (Figure 1 and Section S2). For electroneutrality, the sulfur homocycle has to have a charge of +1 and thus has to be an $[S_8]^{\bullet +}$ radical cation. An alternative interpretation with a different charge distribution (a neutral S_8 ring co-crystallized with $M^+[B_{12}Cl_{12}]^-$ (M = Na, Cs)) can be excluded for several reasons. The conformation of the eight-membered sulfur homocycle is very different (see below) from the typical crown structure of neutral S_8. The $B_{12}Cl_{12}$ cluster is undistorted and very close to I_h symmetry and thus in accord with a $[B_{12}Cl_{12}]^{2-}$ dianion whereas a significant Jahn–Teller distortion would be expected for the radical anion $[B_{12}Cl_{12}]^{\bullet -}$.[23]

The crystal structure shows some disorder for the sulfur ring, which was modeled over two sites (see Section S2). The alkali metal cation in the structure was modeled to be a mixture of Cs^+ and Na^+ with a freely refined ratio. The alkali metal cations originate from incomplete metathesis reactions during the preparation of the $[S_x][B_{12}Cl_{12}]$ ($x = 4$, 8) salts (see Section S1.7). Apparently, their presence is crucial for the crystallization process.

The obtained crystal structure represents the first example of a crystallographically characterized homopolyatomic sulfur radical cation. The $[S_8]^{\bullet +}$ radical cation has an *exo–endo* conformation similar to the structure of $[S_8]^{2+}$ but the transannular sulfur···sulfur contact (S3···S7) is significantly elongated from 285 pm in $[S_8]^{2+}$ to 362 pm in $[S_8]^{\bullet +}$.[9a] The experimentally determined structure of $[S_8]^{\bullet +}$ resembles the structure of the calculated lowest-energy isomer of $[S_8]^{\bullet +}$ (Figure 1).[24]

The elongated transannular sulfur···sulfur contact in $[S_8]^{\bullet +}$ compared to $[S_8]^{2+}$ can be explained by a simple treatment of the frontier molecular orbitals (Figure 2). The highest molecular orbital (HOMO) of $[S_8]^{2+}$ is bonding across the ring and thus results in a shortening of the transannular contact.[8d,9a] When a further electron is added to $[S_8]^{2+}$, the lowest unoccupied orbital (LUMO) of $[S_8]^{2+}$ will be occupied. The resulting singly occupied molecular orbital (SOMO) of $[S_8]^{\bullet +}$ is of antibonding nature across the ring, which causes a significant elongation of the transannular sulfur···sulfur

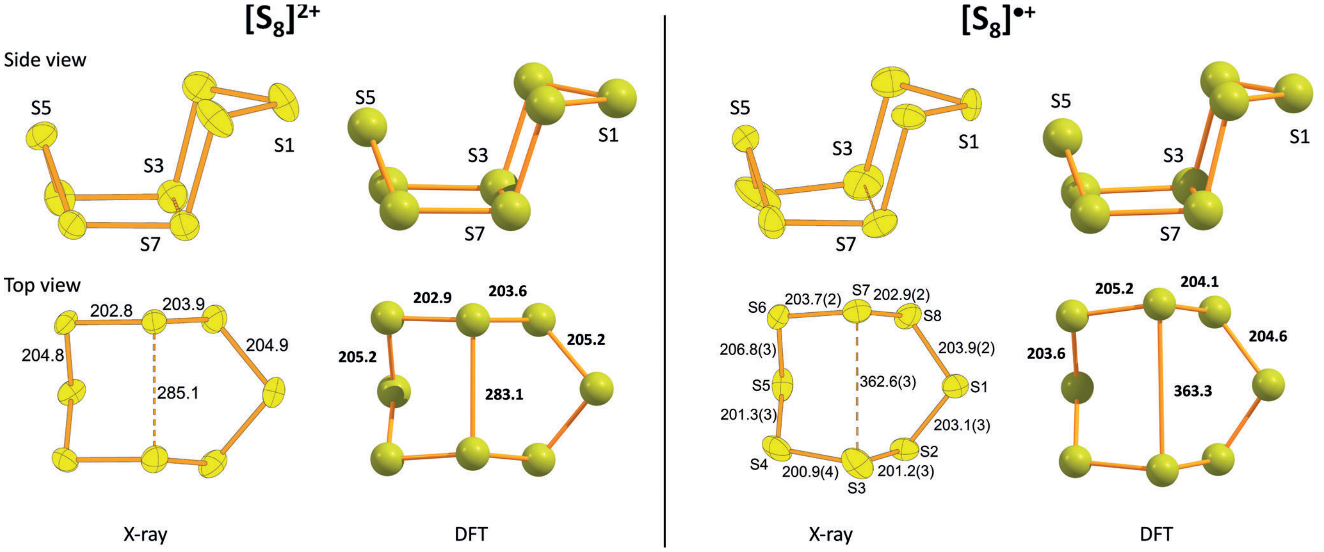

Figure 1. Experimental (X-ray) and calculated (PBE0/def2-TZVPP) structures of $[S_8]^{2+}$ (left) and $[S_8]^{\bullet +}$ (right). Thermal ellipsoids set at 50% probability.

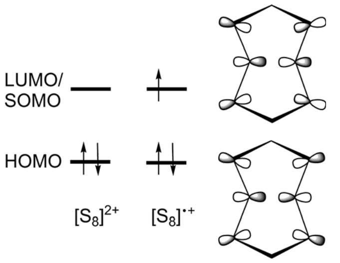

Figure 2. Frontier molecular orbitals of $[S_8]^{2+}$ and $[S_8]^{\bullet+}$.

contact. The experimental structures of $[S_8]^{2+}$ and $[S_8]^{\bullet+}$ were well reproduced by DFT calculations (Figure 1).

The homopolyatomic sulfur radical cation $[S_8]^{\bullet+}$ represents the first step of the oxidation of S_8, and was expected to show an ESR signal. Therefore, we revisited previously published ESR data of homopolyatomic sulfur cations. Solutions of sulfur in superacidic media containing small amounts of a strong oxidizer showed a signal at $g = 2.027$ in ESR spectroscopic investigations.[11] The signal at $g = 2.014$, assigned to $[S_5]^{\bullet+}$, appeared only in the presence of large amounts of strong oxidizers.[17] Symons and co-workers have investigated the sulfur radicals formed by radiation of S_8 in frozen trichlorofluoromethane solution by ESR spectroscopy.[25] They observed two different signals, which were assigned to two different forms of $[S_8]^{\bullet+}$. The initially formed radical with $g_{av} = 2.041$ is transformed into a second radical with $g_{av} = 2.027$ upon annealing. Taking into account the crystal structure data presented above, Symons' experiments can be reinterpreted as follows: Irradiation of S_8 in frozen solution gives $[S_8]^{\bullet+}$ in crown conformation, which is transformed into the lowest-energy isomer with an *exo–endo* conformation, as in the crystal structure, upon annealing. The g value of the relaxed form of the $[S_8]^{\bullet+}$ radical cation in Symons' report is identical to that of the sulfur radical found in initial stages of the oxidation of sulfur in superacidic media. Therefore, it is very likely that the first step of the oxidation of sulfur in superacidic media also corresponds to the formation of the $[S_8]^{\bullet+}$ radical cation.

To assess the thermodynamic stability of homopolyatomic sulfur cations with an average oxidation state of sulfur between $+{}^1/_8$ and $+{}^1/_4$ in SO_2 solution, the free reaction energies of the respective equilibria including solvation energies were calculated (Table 1 and Section S3). All disproportionation reactions considered for $[S_8]^{\bullet+}$ are endergonic. Thus $[S_8]^{\bullet+}$ is a thermodynamically stable radical cation in solution. In contrast, $[S_7]^{\bullet+}$ and $[S_6]^{\bullet+}$ disproportionate into $[S_5]^{\bullet+}$ and $[S_8]^{\bullet+}$. These calculations also suggest the presence of $[S_5]^{\bullet+}$ in solution. Therefore, solutions with sulfur in oxidation states between $+{}^1/_8$ and $+{}^1/_4$ very likely contain two different sulfur homopolyatomic cations, namely $[S_5]^{\bullet+}$ and $[S_8]^{\bullet+}$. These findings are in perfect agreement with ESR spectroscopic investigations[10a,11,13,16,17,25] and the herein presented crystal structure of a salt containing an $[S_8]^{\bullet+}$ radical cation.

In conclusion, crystallographic evidence has been presented that the first step of the oxidation of elemental sulfur, S_8, is actually the formation of the hitherto unknown $[S_8]^{\bullet+}$ radical cation.

Table 1: Reaction enthalpies and free energies [kJ mol^{-1}] in the gas phase and SO_2 solution determined by quantum-chemical calculations (PBE0/def2-TZVPP).

Oxidation state	Equation	$\Delta H_{(gas)}$	$\Delta H_{(SO_2)}$	$\Delta G_{(SO_2)}$
$+{}^1/_8$	$\mathbf{[S_8]^{\bullet+}} \rightleftarrows [S_7]^{\bullet+} + {}^1/_8\,S_8$	24.6	17.6	11.2
	$\mathbf{[S_8]^{\bullet+}} \rightleftarrows [S_6]^{\bullet+} + {}^2/_8\,S_8$	43.8	31.5	21.6
	$\mathbf{[S_8]^{\bullet+}} \rightleftarrows [S_5]^{\bullet+} + {}^3/_8\,S_8$	49.4	26.4	6.8
	$\mathbf{[S_8]^{\bullet+}} \rightleftarrows [S_4]^{\bullet+} + {}^4/_8\,S_8$	112.8	77.9	118.8
	$\mathbf{[S_8]^{\bullet+}} \rightleftarrows {}^4/_8\,[S_8]^{2+} + {}^4/_8\,S_8$	201.5	40.7	47.8
$+{}^1/_7$	$[S_7]^{\bullet+} \rightleftarrows \mathbf{{}^2/_3\,[S_8]^{\bullet+}} + \mathbf{{}^1/_3\,[S_5]^{\bullet+}}$	−8.2	−8.8	−9.0
$+{}^1/_6$	$[S_6]^{\bullet+} \rightleftarrows \mathbf{{}^1/_3\,[S_8]^{\bullet+}} + \mathbf{{}^2/_3\,[S_5]^{\bullet+}}$	−10.9	−13.9	−17.1
	$[S_6]^{\bullet+} \rightleftarrows \mathbf{{}^1/_2\,[S_5]^{\bullet+}} + \mathbf{{}^1/_2\,[S_7]^{\bullet+}}$	−6.9	−9.5	−12.6
$+{}^1/_5$	$\mathbf{[S_5]^{\bullet+}} \rightleftarrows {}^3/_{10}\,[S_6]^{2+} + {}^2/_5\,[S_8]^{\bullet+}$	108.3	20.9	41.2

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Conflict of interest

The authors declare no conflict of interest.

Keywords: crystal structures · homopolyatomic cations · radicals · sulfur · weakly coordinating anions

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[22] See Section S2. Further details on the crystal structure investigations may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: (+49)7247-808-666; e-mail: crysdata@fiz-karlsruhe.de), on quoting the depository number CSD-432497.

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Communications

Sulfur

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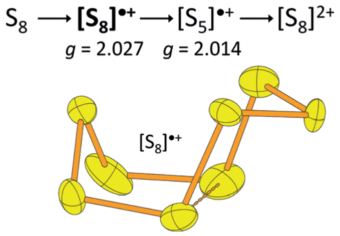
The First Step of the Oxidation of Elemental Sulfur: Crystal Structure of the Homopolyatomic Sulfur Radical Cation $[S_8]^{\bullet+}$



A radical step: Crystallographic evidence is presented for the new homopolyatomic sulfur radical cation $[S_8]^{\bullet+}$, which is the product of the first step of the oxidation of elemental sulfur. These results are supported by quantum-chemical calculations and confirm previously published ESR data.