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Isolation and characterization of a non-rigid hexamethylbenzene-SO\(^{2+}\) complex

Moritz Malischewski\[^a,[b]\] and Konrad Seppelt\[^a]\]

In memoriam of George Olah (1927-2017)

**Abstract:** During our preparation of the pentagonal-pyramidal hexamethylbenzene-dication \(\text{C}_6(\text{CH}_3)_6^{2+}\) we isolated the unprecedented dicatonic species \(\text{C}_6(\text{CH}_3)_6\text{SO}^{2+}\) (AsF\(_5\)_2) from the reaction of hexamethylbenzene with a mixture of anhydrous HF, AsF\(_5\) and liquid SO\(_2\). This compound can be understood as a complex of unknown SO\(^{2+}\) with hexamethylbenzene. Herein, we report the synthesis, its molecular structure and its spectroscopic characterization.

Sulfur dioxide SO\(_2\) is a toxic gas, which is annually produced in million ton scale during the production of sulfuric acid. Aqueous solutions of SO\(_2\) are weakly acidic and behave as a reducing agent, in contrast, anhydrous SO\(_2\) (boiling point -10°C) can be used as an extremely oxidation-stable solvent (up to nearly +6 V vs. standard hydrogen electrode).\[^1]\] In the past years, activation of small molecules has become an important research field in inorganic chemistry, although reports on the reactivity of SO\(_2\) are scarce. The most successful approach so far has been the use of frustrated Lewis pairs\(^{2,3}\) to overcome the weak nucleophilicity of SO\(_2\) which even allows its use as a solvent in superacid chemistry. For instance, Gillespie stated that SO\(_2\) is not protonated to a significant extent in magic acid (HSO\(_3\)F/AsF\(_5\))\.\[^4\] However, Kornath reported 30 years later the formation of [FS(OH)]\(_2\)\(^+\) SbF\(_5\) from the reaction of SO\(_2\) with HF/AsF\(_5\)\.\[^5\]

In order to oxidize hexamethylbenzene \(\text{C}_6(\text{CH}_3)_6\) to its pentagonal-pyramidal dication \(\text{C}_6(\text{CH}_3)_6^{2+}\)\.\[^6\] we used the powerful oxidant and Lewis acid AsF\(_5\) in a mixture of anhydrous HF and liquid SO\(_2\) as solvent. Surprisingly, instead of the desired product, orange crystals of \(\text{C}_6(\text{CH}_3)_6\text{SO}^{2+}\) (AsF\(_5\)_2) could be isolated in the cold from the orange-red solution. In the absence of the superacid HF/AsF\(_5\) no reaction is observed. When colourless hexamethylbenzene is dissolved in pure SO\(_2\) only a yellow solution is obtained, probably due to the formation of a weak charge-transfer complex. The increased electron density on the oxygen atoms of SO\(_2\) in this complex enhances the proton affinity of SO\(_2\) (see supporting information for further details) and therefore facilitates protonation by the superacid HF/AsF\(_5\) which leads to the abstraction of one oxygen atom as H\(_2\)O\(^+\). Consequently, SO\(_2\) is formally cleaved into SO\(^{2+}\) and O\(^+\). The former binds to the electron-rich hexamethylbenzene while the latter is consumed by the (super)lewis acid.

However, under the reaction conditions no pure material is obtained since side reactions occur (e.g. protonation of hexamethylbenzene) which complicate the spectroscopic characterization. Due to the sensitivity of the complex no work besides recrystallization directly from the reaction mixture is possible. Although \(\text{C}_6(\text{CH}_3)_6\text{SO}^{2+}\) (AsF\(_5\)_2) is the main component of the isolated material, ionic side-products co-precipitate due to their low solubility in HF at low temperatures.

\[
\text{C}_6(\text{CH}_3)_6 + \text{SO}_2 + 3 \text{AsF}_5 + 3 \text{HF} \rightarrow [\text{C}_6(\text{CH}_3)_6\text{SO}^{2+}\text{(AsF}_5\text{)}_2 + \text{H}_2\text{O}^+ \text{AsF}_5^-.]
\]

**Figure 1.** Preparation of \(\text{C}_6(\text{CH}_3)_6\text{SO}^{2+}\) (AsF\(_5\)_2)

\(\text{C}_6(\text{CH}_3)_6\text{SO}^{2+}\) (AsF\(_5\)_2) crystallizes in the triclinic space group P-1. The dication consists of an almost planar benzene ring capped by a sloped SO fragment. The sulfur atom is coordinated to a pentagonal dication C\(_6\) and hexamethylbenzene (1.411(1) Å)\.\[^7\]

The carbon-sulfur distances are 2.121(3) and 2.167(3) Å and therefore significantly longer than carbon-sulfur single bonds in thirane (ethylene sulfide) with 1.82 Å\.\[^8\] Interestingly, the C-S-C bond angle is compressed to 39.69(14)° and therefore even smaller than in three-membered thiranium and thiranium salts (40.9(1)-47.6(2)°)\.\[^9\] The distance between the sulfur atom and the benzene plane is 1.941 Å while it is 2.110 Å to the benzene centroid. This indicates that at least in the solid state the SO ligand is not located symmetrically in the middle of the benzene ring. The other carbon-sulfur distances are in the range of 2.376-2.991 Å and therefore significantly below of the sum of van-der-Waals radii (3.5 Å)\.\[^10\]

**Figure 2.** Molecular Structure of \(\text{C}_6(\text{CH}_3)_6\text{SO}^{2+}\), S yellow, O red, C grey, H white

The sulfur-oxygen bond length of 1.424(2) Å is characteristic for a relatively short S-O double bond\.\[^11\] This value is lower compared to the double bond in free SO (1.481 Å, triplet ground state, isovalence-electronic to O\(_2\))\.\[^12\] but higher than the calculated literature value of 1.39 Å for a triple bond in free SO\(^{2+}\)\.\[^13\] because the charge-transfer into an antibonding S-O orbital of SO\(^{2+}\) lowers the S-O bond order. This trend is additionally reflected by DFT calculations using B3LYP/def2-TZVP (S-O bond length of 1.376 Å for SO\(^{2+}\) and 1.438 Å for \(\text{C}_6(\text{CH}_3)_6\text{SO}^{2+}\)).

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Table 1. Selected geometrical parameters of Cs(CH₃)₂SO⁺ (AsF₆)₂ in the crystal

<table>
<thead>
<tr>
<th>Geometrical parameter</th>
<th>Cs(CH₃)₂SO⁺ (AsF₆)₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-C bond lengths (benzene ring)</td>
<td>1.396(6)-1.438(5) Å</td>
</tr>
<tr>
<td>C-S bond distances</td>
<td>2.121(3), 2.167(3) Å</td>
</tr>
<tr>
<td>C-S-C bond angle</td>
<td>39.69(14)°</td>
</tr>
<tr>
<td>S-O bond length</td>
<td>1.424(2) Å</td>
</tr>
</tbody>
</table>

DFT calculations for the S-O vibration using B3LYP/def2-TZVP predicted a value of 1266 cm⁻¹ for the SO⁺ adduct, and 1541 cm⁻¹ for free SO⁺, respectively, indicating a lower bond order for the charge-transfer complex. The S-O vibration of free SO is experimentally known (1137 cm⁻¹). [14]

An IR-spectrum of the isolated material revealed a strong band at 1250 cm⁻¹ which can be assigned to the S-O stretch vibration. [15]

Table 2. Comparison of experimental and calculated S-O distances for Cs(CH₃)₂SO⁺, SO and SO²⁺

<table>
<thead>
<tr>
<th>Compound</th>
<th>S-O distance in Å (exp.)</th>
<th>S-O distance in Å (calc.)</th>
<th>S-O vibration in cm⁻¹ (exp.)</th>
<th>S-O vibration in cm⁻¹ (calc.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cs(CH₃)₂SO⁺</td>
<td>1.424</td>
<td>1.438</td>
<td>1250</td>
<td>1266</td>
</tr>
<tr>
<td>SO</td>
<td>1.481</td>
<td>1.490</td>
<td>1137</td>
<td>1159</td>
</tr>
<tr>
<td>SO²⁺</td>
<td>------</td>
<td>1.376</td>
<td>------</td>
<td>1541</td>
</tr>
</tbody>
</table>

In contrast to SO₂ or SO₃, lower-valent sulfur oxides are generally unstable. Free SO even decomposes in high dilution in the gas phase within short time [16] but can be detected in interstellar space. [17] Interestingly, SO can be stabilized as a ligand in the coordination sphere of metal complexes. [18-19] In general, the µ² bridging mode [20] is much more often observed than SO as a terminal [21] or µ³ bridging ligand. [22] Recently, adduct formation of SO with carbenes has been reported. [23-24]

For SO²⁺, which is iso-valence-electronic to N₂, CO and NO⁺, literature reports are extremely rare. In the 1990s Jander discussed the autodissociation of liquid SO₂ into SO⁺ and SO²⁺. [25] Later reports claimed the existence of solvated SO²⁺ from the reaction of thionyl chloride and silver salts in acetone [26] and from autodissociation of thionyl chloride in DMF. [27] Under strongly ionizing conditions, SO²⁺ has been detected in the gas phase. [28]

Although the detection of the Cs(CH₃)₂SO⁺ adduct is unprecedented, the general structure is not. Already in the 1980s, the formation of a charge-transfer complex between NO⁺ and hexamethylbenzene was observed. [29] NO⁺ is coordinated to two carbon atoms of an aromatic C-C bond and tilted in respect to the benzene plane. The distance between the nitrogen atom and the benzene plane is with 2.07 Å slightly longer than in the SO²⁺ adduct. The N-O bond in [Cs(CH₃)₂NO⁺ SbF₆] (1.108(2) Å) [7-26] is slightly elongated compared to NO⁺ (1.062(4) Å). [31]

The similarity between the NO⁺ and SO²⁺ adducts is reflected by ¹⁳C NMR spectra. While the two signals of hexamethylbenzene shift from δ 17.0 and 133.2 ppm to 17.8 and 150.8 ppm in the NO⁺ complex, [30] the SO²⁺ adduct gives two signals at δ 20.8 and 165.5 ppm (measured in SO₂ at -70°C) which proves the dynamic nature of the complex as well as the deshielding of the carbon atoms of the benzene ring.

This dynamic behaviour can be described with three different structures: a three-membered ring, a Cs₆ symmetric transition state and a pyramidal isomer. According to theoretical calculations with MP2/cc-pVTZ the energy difference between these isomers for Cs(CH₃)₂SO°⁺ is ≤ 1 kJ/mol (see supporting information). This calculated barrier would be one of the smallest known for fluxional molecules. [32] So the SO moiety can move practically without barrier over the benzene ring. Consequently, the same should be true for Cs₆H₆SO⁺ since Cs₆H₆NO⁺ is also known to have a very flat potential energy surface. [33] For comparison, ethane CsH₆ has a rotational barrier of about 13 kJ/mol. The heavier homologues Cs₆H₆ and Ge₆H₆ have rotational barriers of about 4 and 3 kJ/mol. [34]

In summary, C₆(CH₃)₆SO⁺ (AsF₆)₂ can be prepared from the reaction of hexamethylbenzene with a mixture of anhydrous HF, AsF₆ and liquid SO₂. Although [Cs(CH₃)₂SO⁺] can only be handled in SO₂ or HF (due to decomposition in organic solvents) its existence suggests the possibility of stabilizing highly electrophilic small molecules as charge-transfer complexes with permethylated arenes. The SO moiety is supposed to migrate over the benzene ring with almost no energetic barrier.

Experimental Section

The reaction is performed in PFA tubes (tetrafluoroethene-perfluoroalkoxyvinyl-copolymer) connected to stainless steel valves / stainless steel vacuum line. Attention: SO₂, HF and AsF₆ are highly toxic gases which should only be handled by trained personal in appropriate equipment.
Thionylhexamethylenbenzenium(2+)-hexafluoroarsenate
Thionyliumhexamethylenbenzenium(2+)-hexafluoroarsenate

41 mg (0.25 mmol) hexamethylenbenzene are filled into a 8 mm PFA-tube. 0.6 g SO$_3$ are condensed in at -196°C. The mixture is thawed to obtain a yellow solution. Subsequently, the mixture is cooled to -196°C and 2.4 g anhydrous HF and 0.2 g (1.2 mmol) AsF$_5$ are condensed in. The tube is sealed off and placed in a -75°C freezer. After one day, the tube is brought to room temperature and shaken for some minutes (Attention: overpressure!) and then placed again in the freezer. After several days orange needles are obtained in the orange-red solution. The crystals are decanted off in the sealed tube by turning the tube carefully upside down, the mother liquor is frozen with liquid nitrogen. The tube is opened with a scissor and the open tube containing the crystalline material is connected to a steel valve and dried in vacuum, the mother liquor is discarded (Attention: Danger!). The amount of isolated product is low to moderate.

NMR (SO$_3$: -70 °C, unlocked) $^1$H: δ 3.13 ppm (s, br, 18H); 10.36 ppm (s, br, H$_2$O$^-$)
$^1$C$^+$(H): δ 20.76 ppm (CH$_2$, 6 C), 165.46 ppm (ring, 6 C)
IR in cm$^{-1}$: 2915, 1592, 1516, 1433, 1377, 1338, 1250, 1076, 1028, 990, 962, 693, 671

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Keywords: carbocation • electron-deficient compounds • superacid • hypercoordination • oxidation

References


CCDC 1566140 contains the crystallographic information for this publication. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.
The unprecedented complex $C_6(CH_3)_6SO_2^+$ (AsF$_5$)$_2$ is isolated from the reaction of hexamethylbenzene with SO$_2$, anhydrous HF and AsF$_5$.

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