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Polysulfates

The Elusive Tetrasulfate Anion $[S_4O_{13}]^{2-}$**

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It is well-established that condensation reactions of sulfuric acid lead successively to polysulfuric acids; that is, disulfuric acid, trisulfuric acid, and so on. This condensation leads finally to asbestos-type SO_3 (α-SO_3 and β-SO_3), which is a polysulfuric acid according to $H(SO_3)_nOH$, but with very large numbers for n. The backbone of the polysulfuric acids are vertex-connected $\{SO_4\}$ tetrahedra, and the simplest species, with $n=2$ in the above formula, is disulfuric acid, $H_2S_2O_7$. Astonishingly, the latter is the only condensation product of H_2SO_4 for which a detailed structure is known,[1] and acids with $n>2$ have not been investigated to date. The situation is only marginally better concerning the salts of polysulfuric acids. Knowledge is essentially restricted to about 20 well-characterized disulfates.[2] Furthermore, the trisulfate $(NO_2)[S_3O_{10}]$ was reported in 1954 by MacGillavry et al. as reaction product of N_2O_5 and SO_3.[3] The structure was solved from X-ray film data, and the space group of the crystals was later corrected by Cruickshank.[4] Even if the crystal structure seems to be erroneous and probably needs revision, the existence of the trisulfate anion $[S_3O_{10}]^{2-}$ in that compound is quite certain. We were recently able to prepare a second trisulfate, $Pb[S_3O_{10}]$, the structure of which was fully characterized.[5] One further polysulfate, $K_2S_5O_{16}$, has been reported in 1969, and its structure has been determined based on X-ray photographs, revealing the presence of the pentasulfate ion, $[S_5O_{16}]^{2-}$.[6] Nevertheless, it must be stated that detailed and comprehensive knowledge of polysulfuric acids and polysulfates is still lacking. Recently we started investigating in more detail the ability of oleum to act as reaction medium for the syntheses of new sulfates.[7] It turned out that SO_3-rich oleum (up to 65 % SO_3) usually leads to the formation of disulfates. Attempting to proceed towards higher polysulfates we expanded these investigations also to reactions with neat SO_3, and adopting the above mentioned reaction of MacGillavry, some of these experiments were carried out with N_2O_5 as reaction partner. Up to now we have used N_2O_5 especially as a nitrating reagent,[8] but it is also a convenient source for NO_2^+ cations. Herein we present the synthesis and structure of $(NO_2)_2[S_4O_{13}]$, which is the first tetrasulfate reported and, furthermore, only the second polysulfate for which structural details have become available by state-of-the-art X-ray data.

There are four crystallographically different $[S_4O_{13}]^{2-}$ anions in the crystal structure of $(NO_2)_2[S_4O_{13}]$. Their charge is balanced by eight NO_2^+ cations, which all show typical N−O distances of about 110 pm and angles O-N-O that deviate by a maximum of 2.9° from linearity. The tetrasulfate anions are also essentially identical with each other so that their structural features can be discussed on averaged values for bond distances and angles. The bond lengths S−O to the terminal oxygen atoms fall in the typical narrow range of 141 to 143 pm (Figure 1). However, the distances within the S-O-S bridges are remarkable: The linkage of the inner two tetrahedra, represented by S2 and S3, occurs by the S2-O7-S3 bridge, which is quite symmetrical with respect to the distances S2−O7 (163.9 pm) and S3−O7 (160.9 pm). In contrast, the connection of the terminal tetrahedra (S1 and S4, respectively) is realized by strongly asymmetric bridges with distances of about 153 (S2−O4 and S3−O10) and 177 pm (S1−O4 and S4−O10). These unusually long distances cause also severe distortions from the tetrahedral shape of the terminal $\{SO_4\}$ moieties, which can be rationalized as shifts of the sulfur atoms S1 and S4 towards the triangular faces built up by the oxygen atoms O1, O2, O3 and O11, O12, O13, respectively. Accordingly, the angles O-S-O

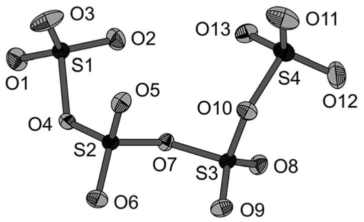

Figure 1. Structure and atom labeling of the $[S_4O_{13}]^{2-}$ anion. Ellipsoids are set at 75 % probability. In the crystal structure there are four crystallographically different but structurally almost identical anions. Selected bond lengths [pm] and angles [°] are given as averaged values for the four anions (calculated values *in italics*): S1–O1 142.0/*144.6*, S1–O2 142.3/*144.3*, S1–O3 142.3/*144.5*, S1–O4 176.6/*183.4*, S2–O4 153.0/*154.5*, S2–O5 141.4/*143.2*, S2–O6 141.1/*143.5*, S2–O7 163.9/*165.0*, S3–O7 160.9/*164.9*, S3–O8 141.3/*143.5*, S3–O9 142.0/*143.2*, S3–O10 153.4/*154.5*, S4–O10 177.0/*183.2*, S4–O11 142.1/*144.5*, S4–O12 143.1/*144.4*, S4–O13 143.1/*144.6*; S1-O4-S2 124.3/*123.9*, S2-O7-S3 122.1/*121.7*, S3-O10-S4 123.7/*123.9*. A detailed list of all data can be found in the Supporting Information, Tables S4 and S6.

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Supporting information for this article, including crystallographic data (measurement and refinement procedures, atom coordinates, bond lengths and angles, anisotropic displacement parameters), theoretical data for the polysulfate anions $[S_nO_{3n+1}]^{2-}$, $n=2$–11 (atom coordinates, bond lengths, energies, Raman frequencies), and a color figure of the crystal structure, is available on the WWW under http://dx.doi.org/10.1002/anie.201108206.

involving these oxygen atoms lie between 115 and 117° and thus approach the value of 120° that would result if the sulfur atoms are at the center of the triangular faces. The latter situation would suggest the description in the Lewis acid–base formalism with two SO_3 molecules as Lewis acids attached to a disulfate anion as Lewis base; that is, according to $[S_2O_7]^{2-}\cdot 2\,SO_3$ instead of $[S_4O_{13}]^{2-}$.

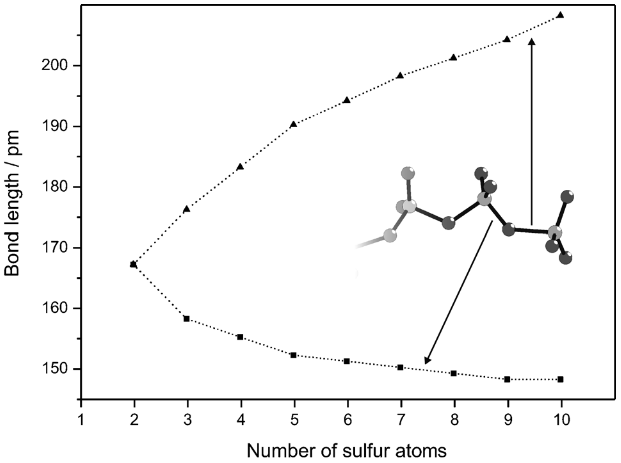

Figure 2. Dependence of the distances S–O within the terminal S-O-S bridges of the polysulfates $[S_nO_{3n+1}]^{2-}$ with an increasing number n of sulfur atoms. The values were extracted from theoretical calculations at the PBE0/cc-pVTZ level of theory.

It is interesting to compare the findings for $[S_4O_{13}]^{2-}$ with the reported bond lengths within the S-O-S bridges of the polysulfates known to date. In the trisulfate $Pb[S_3O_{10}]$, the S-O-S bridges differ within the S–O bonds by 14 pm, while the pentasulfate $K_2[S_5O_{16}]$ have bond lengths within these bridges of 151 and 182 pm (Table 1). This means that the asymmetry of the S-O-S bridges to the terminal tetrahedra of the chain increases with the length of the polysulfate anion. To test that assumption, we have performed theoretical investigations on the polysulfates $[S_nO_{3n+1}]^{2-}$ up to $n=11$ using density functional theory (PBE0), and furthermore perturbation theory (MP2) for $n=2$–8. The results corroborate the experimental findings for the polysulfates known to date very well (Table 1). Although the calculated bond lengths are typically longer than the observed values if the calculation is performed on negatively charged species, the tendency of increasing asymmetry within the S-O-S bridges is well reproduced and shows that this is an intrinsic feature of the anions and not caused by solid state effects. The calculations on the previously hypothetical polysulfates with $n=6$–11 show that the asymmetry becomes even more dramatic with growing chain lengths, and the distances S–O for $n=10$ are 148 and 208 pm (Figure 2). In line with these observations, the respective mean bond lengths S–O for the terminal oxygen atoms decrease from 146.1 pm for the disulfate anion $[S_2O_7]^{2-}$ ($n=2$) to 143.5 pm in $[S_{11}O_{34}]^{2-}$. The later value is close to the bond length reported for molecular SO_3,[9] and is another argument for the interpretation of the polyanions as Lewis acid–base complexes. The bond length changes are also reflected by the Raman frequencies of the polyanions. Although their vibration modes are quite complex and usually combinations of several vibrations, the most characteristic modes show a clear blue-shift for the stretching vibrations with decreasing bond distances.[10]

Table 1: Bond lengths[a,b] [pm] within the terminal S-O-S bridges for polysulfates $[S_nO_{3n+1}]^{2-}$ with $n=3$, 4, 5.

$Pb[S_3O_{10}]$[5]		$(NO_2)_2[S_4O_{13}]$		$K_2[S_5O_{16}]$[6]	
expt.	theor.	expt.	theor.	expt.	theor.
155.3/169.4	158.3/175.8	153.4/177.0	154.5/183.2	150.7/182.6	152.1/189.9
155.3/169.4	158.3/175.8	153.0/176.6	154.5/183.4	150.7/182.6	152.1/189.9

[a] Extracted from density functional calculations on the PBE0/cc-pVTZ level. [b] Distances are given for both ends of the anions; the calculations were performed without symmetry restrictions.

The stabilization energy of the anions decreases with increasing values for n. However, they are negative in all cases, thus showing stability even for large anions up to $n=11$ (Figure 3). In contrast, the Gibbs free stabilization enthalpies derived from the calculations for $T=298$ K are only negative up to $n=10$, while for the largest anion under investigation it becomes slightly positive (Figure 3). It should be mentioned that the costly and time-consuming MP2 calculations deliver essentially the same values as found with DFT theory. Nevertheless theoretical calculations assuming gas-phase conditions cannot deliver "true" thermodynamical values. Even if the tendency of decreasing stability of the anions with their increasing chain lengths is certainly correct, we started to perform calculations that take solvation effects into account (for example, the models PCM or COSMO)[11] and will give a more detailed view of these anions.

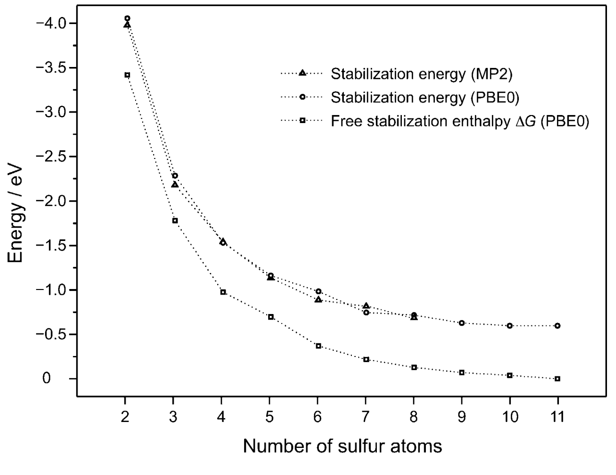

Figure 3. Stabilization energies and free stabilization enthalpies of the polysulfates $[S_nO_{3n+1}]^{2-}$ with increasing number n of sulfur atoms. The values were extracted from density functional calculations at the PBE0/cc-pVTZ level. For $n=2$–8, the density functional calculations were validated using perturbation theory at the MP2/cc-pVTZ level. The nearly perfect correlation of the values indicates that the energies obtained for $n>7$ are highly reliable, even when they are not validated.

It is instructive that the curve of the calculated stabilization energy in Figure 3 reflects very well our present knowledge on polysulfates. On the other hand, this gives clear hint that higher polysulfates should be possible to synthesize. Low temperatures seem to be mandatory, and weakly coordinating cations causing low polarization of the anions should be the counter ions of choice. Following these lines we are currently investigating the system N_2O_5/SO_3 in great detail, and we are convinced that the discovery of further polysulfates will confirm our theoretical findings. Furthermore, we are trying to improve the latter by implementing solvation effects into the calculations. Finally, it would be of particular interest to also obtain the free polysulfuric acids, which are not known at all to date. We hope that this work might also inspire others in shedding additional light on this fundamental class of compounds.

Experimental Section

$(NO_2)_2[S_4O_{13}]$: N_2O_5 was prepared according to a literature procedure.[12] SO_3 was prepared by distillation of fuming sulfuric acid over P_4O_{10} at 140 °C. N_2O_5 was then sublimated into a liquid nitrogen cooled glass tube ($d = 16$ mm, $l = 300$ mm). Thereupon a large excess of SO_3 was sublimated under the same temperature conditions. The tube was torch-sealed under vacuum, placed in a resistance furnace, and heated to 80 °C. This temperature was maintained for 24 h. Upon slow cooling ($0.5\,°C\,h^{-1}$), a number of colorless and extremely moisture-sensitive single crystals are obtained. **Caution**! During the reaction and even after cooling down to room temperature, the glass tubes might be under pressure. The tubes have to be protected with an explosion shield during reaction and should be cooled with liquid nitrogen before they are opened.

Several single crystals of $(NO_2)_2[S_4O_{13}]$ were selected under protecting oil with the help of a polarization microscope and directly transferred into the cool nitrogen stream (153 K) of a single-crystal diffractometer (BRUKER APEX II). After unit-cell determination, the reflection intensities were collected. $(NO_2)_2[S_4O_{13}]$: colorless blocks ($0.32 \times 0.43 \times 0.50\,mm^3$), monoclinic, $C2/c$, $Z = 32$, $a = 21.1668(7)$, $b = 21.1645(7)$, $c = 23.0839(7)$ Å, $\beta = 102.027(2)°$, $V = 10114.2(6)$ Å^3, $\rho = 2.25\,g\,cm^{-3}$, $2\theta_{max} = 70.3°$, $\lambda(Mo_{K\alpha}) = 71.073$ pm, 153 K, 183219 reflections, 22368 unique reflections ($R_{int} = 0.0534$, $R_\sigma = 0.0339$), numerical absorption correction ($\mu = 8.6\,cm^{-1}$, min./max. transmission = 0.6709/0.7703, programs X-RED 1.22 and X-Shape 1.06: Stoe, Darmstadt, **2001** and **1999**), structure solution by direct methods, full-matrix least-square refinement (830 parameters) on $|F^2|$, (programs SHELXS-97 and SHELXL-97: G. M. Sheldrick, Programs for the solution and refinement of crystal structures, Göttingen, **1997**), $R_1 = 0.0299$, $wR_2 = 0.0813$ for 15854 reflections with $I > 2\sigma(I)$ and $R_1 = 0.0497$, $wR_2 = 0.0868$ for all 22368 reflections, max./min. residual electron density = $0.838/-0.780\,e^-\,Å^{-3}$. 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-423475.

The Raman spectrum was measured (spectrometer FRA106, Bruker, Karlsruhe, Germany) on a number of selected crystals in a small glass tube. Important selected Raman intensities [cm^{-1}] (exptl/*calcd*): 1479/*1421*, 1471/*1409*, 1399/*1352*, 1257/*1245*, 1213/*1207*, 1073/*1082*, 978/*934*, 851/*792*, 719/*748*, 649/*649*, 584/*592*, 555/*570*, 533/*549*, 454/*431*, 373/*398*, 328/*324*, 262/*290*, 232/*267*.

Throughout the study, the Gaussian 03 program package was used,[13] and the vibrational frequencies were scaled by a factor of 0.96.[14] Full geometry optimizations of the polysulfates $[S_nO_{3n+1}]^{2-}$ were performed using the PBE0 functional for exchange and correlation within density functional theory for $n = 2$–11. In all calculations, a cc-pVTZ basis was used although convergence checks up to quintuple zeta basis sets have been performed. Furthermore, the influence of diffuse functions on the results has been studied. The DFT calculations were validated by corresponding MP2 calculations for $n = 2$–7. Apart from the geometry optimization, the stabilization energy and free stabilization enthalpy at $T = 298$ K were calculated for a given polysulfate containing n sulfur atoms for the reaction $[S_{n-1}O_{3n-2}]^{2-} + SO_3 \rightarrow [S_nO_{3n+1}]^{2-}$.

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[10] This is especially observable for the asymmetric S=O stretching vibrations of the terminal tetrahedral and stretching vibrations within the terminal S-O-S bridges. Detailed Raman frequencies of all of the species under investigation can be found in the Supporting Information, Table S10.

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