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$ReO_2Cl(S_2O_7)$, a Molecular Disulfate**

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The tendency of sulfuric acid to form polysulfates as condensation products is not as pronounced as for the less acidic neighbors in the periodic table, H_3PO_4 and H_4SiO_4, for which numerous polyphosphates and polysilicates are known. Therefore, it is not surprising that the number of structurally characterized polysulfates is rather low. Only the alkaline metals Na, K, Cs,[1–3] the main-group elements Se, Sb, Te,[4–6] and the transition-metal Cd form simple "binary" (hydrogen) disulfates,[7] and their crystal structures have been established. The disulfates of Na, K, Cs, and Cd are doubtless true ionic compounds, while $Se_4(HS_2O_7)_2$ and $(IO_2)_2(S_2O_7)$ contain the polyatomic cations Se_4^{2+} and IO_2^+ exhibiting covalent bonds.[4,8] At first glance the disulfates $Sb_2(S_2O_7)_3$ and $Te(S_2O_7)_2$ seem to consist of discrete $Sb_4(S_2O_7)_6$ and $Te(S_2O_7)_2$ molecules, respectively. But if weaker Sb–O (> 240 pm) and Te–O (> 270 pm) contacts are considered, which are clearly within bonding distance, the chain structures of the compounds are revealed. Thus, the only crystallographically characterized molecular disulfate is disulfuric acid, $H_2S_2O_7$.[9] Although molecular derivates of $H_2S_2O_7$ such as the methyl or trimethylsilylester have been prepared, their solid-state structures remain unknown.[10,11] An unambiguous molecular metal disulfate has not been reported to date. During our investigations of refractory metal compounds containing complex oxo anions,[12–14] we also studied the reactions of rhenium metal and rhenium compounds with sulfuric acid/SO_3 mixtures. It turned out that rhenium metal is oxidized by sulfuric acid containing 65% SO_3 to give the Re^{VII} sulfate $Re_2O_5(SO_4)_2$, which adopts two modifications.[12] The compound can be obtained even more conveniently when $Re_2O_7(H_2O)_2$ is used as starting material instead of the metal. Herein, we present the oxide chloride disulfate $ReO_2Cl(S_2O_7)$, which forms in the reaction of $ReCl_5$ with SO_3-rich (65%) oleum in sealed glass ampoules at 150 °C, that is, by the oxidation of Re^V, most probably according to Equation (1).

$$ReCl_5 + 2\,H_2SO_4 + SO_3 \rightarrow ReO_2Cl(S_2O_7) + 4\,HCl + SO_2 \qquad (1)$$

The reaction afforded $ReO_2Cl(S_2O_7)$ in the form of light yellow thin plates that are not only extremely moisture sensitive but start to decompose even under inert conditions when the ampoule was opened. The crystal structure of $ReO_2Cl(S_2O_7)$ exhibits discrete C_i-symmetrical $Re_2O_4Cl_2(S_2O_7)_2$ molecules that consist of two disulfate-bridged $ReO_2Cl(S_2O_7)$ monomers (Figure 1). The rhenium atoms are in distorted octahedral coordination with two terminal oxide ligands featuring short Re=O distances of 168 and 169 pm and an angle O=Re=O of 103°, one chloride ion in *cis* position to O=Re=O, and two disulfate groups. A ReO_2 moiety of similar geometry is found in the oxidochloridorhenates(VII) $Cs[ReO_2Cl_4]$ and $[(C_2H_5)_4P][ReO_2Cl_4]$.[15,16] The distance Re–Cl in $ReO_2Cl(S_2O_7)$ (223 pm) is about 10 pm shorter than the corresponding bonds in the $[ReO_2Cl_4]^-$ anion.

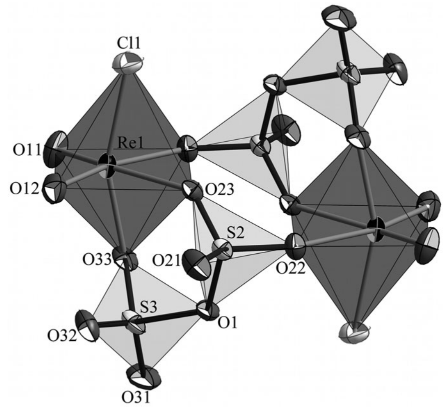

Figure 1. Structure and atom labeling of the C_i-symmetrical $Re_2O_4Cl_2(S_2O_7)_2$ molecule. Thermal ellipsoids are set at 75% probability. Selected bond lengths [pm] and angles [°] (calculated values in italics): Re1–O11 167.8(4)/*166.01*, Re1–O12 168.6(4)/*165.88*, Re1–O33 200.0(4)/*195.59*, Re1–O23 216.7(4)/*216.26*, Re1–O22 218.6(3)/*217.39*, Re1–Cl1 222.9(2)/*223.89*, S2–O21 141.6(4)/*140.68*, S2–O22 146.9(4)/*146.56*, S2–O23 148.1(4)/*147.87*, S2–O1 162.2(4)/*160.71*, S3–O31 141.4(4)/*140.74*, S3–O32 142.5(4)/*141.37*, S3–O33 154.2(4)/*155.04*, S3–O1 163.7(4)/*163.82*; O11-Re1-O12 103.0(2)/*103.12*, S2-O1-S3 121.7(2)/*123.04*.

The only crystallographically distinguishable disulfate group coordinates asymmetrically to both rhenium atoms of the $Re_2O_4Cl_2(S_2O_7)_2$ molecule. Towards one Re atom, $S_2O_7^{2-}$ acts as a chelating ligand (through oxygen atoms O23 and O33), whereas the second Re atom is coordinated only by

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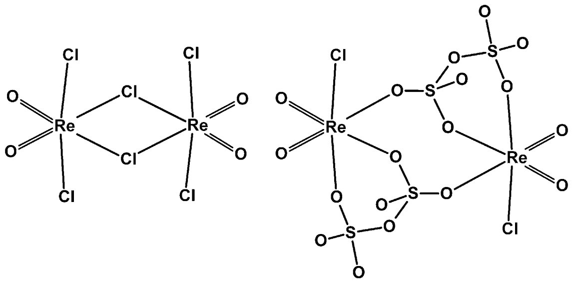
Supporting information for this article, including complete crystallographic data (measurement and refinement procedure, atom coordinates, bond lengths and angles, anisotropic displacement parameters), calculated bond lengths and angles, experimental and calculated Raman vibrational data, a photograph of $ReO_2Cl(S_2O_7)$ crystals, and a visualization of the intermolecular interactions in the crystal structure, is available on the WWW under http://dx.doi.org/10.1002/anie.201105457.

O22 (Figure 1). Due to the structural *trans* effect significant differences in the Re—O bond lengths can be observed:[17] Oxygen atoms located trans to the Re=O bond (O11 and O12) show values of 219 and 217 pm, respectively, while the one in *cis* orientation (O33) is found at 200 pm. These distance variations are reflected by corresponding bond lengths with the disulfate anions: The oxygen atoms exhibiting long Re—O bonds are found at short distances to the sulfur atoms (S2—O22/23 at 147 and 148 pm) while the S3—O33 bond shows a length of 154 pm. Oxygen atoms that do not coordinate to rhenium atoms (O21, O31, O32) have the shortest distances S—O around 142 pm. The angle within the oxygen bridge of the anion S2-O1-S3 is found at 122° and is, as well as the distances S2—O1 (162 pm) and S3—O1 (164 pm), in accordance with reported findings.[1–8]

The observed geometrical parameters of the $Re_2O_4Cl_2(S_2O_7)_2$ molecule are in excellent agreement with the values obtained from calculations at a high level of theory (see caption of Figure 1). In the solid state the molecules are packed in a primitive fashion and held together by weak interactions between rhenium and oxygen atoms of the adjacent molecule (Re—O > 360 pm). The so-called halogen bonding between oxygen and chlorine atoms of neighboring molecules might also play a role.[18,19]

The Raman spectrum of $ReO_2Cl(S_2O_7)$ could be obtained by measuring the substance in a glass ampoule containing a small amount of oleum to avoid decomposition. The spectrum is in very good agreement with its theoretical prediction if some deviations in intensity are neglected (see the Experimental Section).

Interestingly, the structure of the $Re_2O_4Cl_2(S_2O_7)_2$ molecule can be easily deduced from the Re^{VII} oxide chloride ReO_2Cl_3 reported by Seppelt et al. in 2006.[16,20] In the solid state, ReO_2Cl_3 consists of chloride-bridged $Re_2O_4Cl_6$ dimers with an octahedral coordination sphere around each Re atom and ReO_2 moieties similar to those found in $ReO_2Cl(S_2O_7)$. Two chloride ligands are aligned perpendicular on each ReO_2 unit, whereas both bridging chloride ions are coordinated in *trans* positions to the Re=O groups (Scheme 1). The $Re_2O_4Cl_2(S_2O_7)_2$ molecule is derived by a hypothetical substitution of one bridging chloride ligand and one of the chloride ions *cis* to the oxide ligands by one disulfate ion per rhenium atom.



Scheme 1. Structural relationship between ReO_2Cl_3 (left) and $ReO_2Cl(S_2O_7)$ (right): Hypothetical substitution of two chloride ligands in ReO_2Cl_3 by one disulfate ion leads to $ReO_2Cl(S_2O_7)$.

For the oxide chloride, it has been shown that in solution the dimer $Re_2O_4Cl_3$ can be cleaved into the respective monomers because the dimerization energy is very small ($\Delta H = -0.3$ kcal mol^{-1}). According to our calculations, there could be a stable monomer $ReO_2Cl(S_2O_7)$ with the trigonal bipyramidal structure shown in Figure 2. However, the dimerization energy is much higher ($\Delta H = -25.8$ kcal mol^{-1}) so that fragmentation into the monomers is not easy to achieve. Unfortunately, the sensitivity of the compound makes an experimental investigation very difficult. Indeed all attempts to dissolve $ReO_2Cl(S_2O_7)$ in various typical solvents (CH_3CN, pentane, THF, CCl_4) failed, and in any case decomposition of the compound leading to yet undefined products was observed. It turned out that the compound is also not stable in concentrated sulfuric acid. Obviously a high content of SO_3 is needed for stabilization, and we figured out that even in oleum containing 25% SO_3 the disulfate $ReO_2Cl(S_2O_7)$ cannot be obtained. Instead, the new Re^{VII} sulfate $Re_2O_4Cl_4(SO_4)$, with a unique chain structure, was obtained.[21]

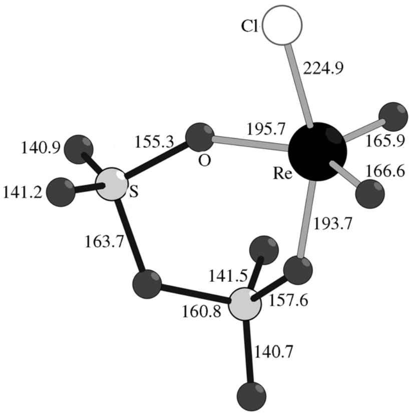


Figure 2. Geometry-optimized structure of the hypothetical monomer $ReO_2Cl(S_2O_7)$. The bond lengths are given in pm.

Currently we are investigating in more detail the high reactivity of $ReO_2Cl(S_2O_7)$ towards organic molecules such as the solvents we used for solvation experiments. It seems to be highly interesting to establish whether this compound could be useful for bond activation. Furthermore we aim for the preparation of $ReO_2Cl(S_2O_7)$ in its hypothetical monomeric form by the reaction of SO_3 and ReO_3Cl.[22] Finally, we are exploring the generalization of the preparative route to achieve access to other sulfates and disulfates that appear to be textbook examples but that are unexplored to date.

Experimental Section

$ReO_2Cl(S_2O_7)$: A solution of $ReCl_5$ (0.3 g) in fuming sulfuric acid (1 mL) containing 65% SO_3 (puriss., Merck, Darmstadt, Germany) was heated in a sealed glass ampoule ($l = 250$ mm, $\varnothing = 20$ mm, $\varnothing$ wall = 2 mm) to 150 °C for 48 h using a block thermostat (Gefran 800P, Liebisch, Bielefeld, Germany). After slow cooling to room temperature (2.5 °C h^{-1}), the product can be isolated in the form of light yellow plates. The crystals of $ReO_2Cl(S_2O_7)$ are highly moisture-sensitive. On air contact, immediate hydrolysis to give a violet liquid takes place. Even in a glove box under inert conditions, the crystals decompose to a violet residue after a short period of time, which is most probably due to the loss of SO_3.

X-ray crystallography: In a glove box, some single crystals were transferred into inert oil (AB128333, ABCR, Karlsruhe, Germany). Under a cooling nitrogen stream a suitable crystal was mounted in a glass capillary ($\varnothing = 0.1$ mm) and placed into a stream of cold N_2 (−120 °C) inside the diffractometer (IPDS I, Stoe, Darmstadt, Germany). After unit cell determination, the reflection intensities were collected. $ReO_2Cl(S_2O_7)$: Light yellow plate ($0.23 \times 0.14 \times 0.08$ mm^3), triclinic, $P\bar{1}$, $Z = 2$, $a = 706.1(1)$, $b = 772.6(1)$, $c = 802.6(1)$ pm, $\alpha = 89.61(2)$, $\beta = 79.62(2)$, $\gamma = 67.35(2)°$, $V = 396.5(1)$ Å^3; $\rho = 3.599$ g cm^{-3}, $2\theta_{max} = 52.28°$, $\lambda(Mo_{K\alpha}) = 71.073$ pm, ϕ scans (2.5°/image), 153 K, 5093 reflections, 1472 unique reflections ($R_{int} = 0.0378$, $R_\sigma = 0.0296$), numerical absorption correction ($\mu = 162.08$ cm^{-1}, min./max. transmission = 0.0907/0.3589. 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 (119 parameters) on $|F^2|$, (programs SHELXS-97 and SHELXL-97: G. M. Sheldrick, Programs for the solution and refinement of crystal structures, Göttingen 1997), $R_1 = 0.0198$, $wR_2 = 0.0465$ for 1352 reflections with $I > 2\sigma(I)$ and $R_1 = 0.0233$, $wR_2 = 0.0476$ for all 1472 reflections, max./min. residual electron density = 0.970/−0.924 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-419178.

Calculations: A full geometry optimization of the dimer $Re_2O_4Cl_2(S_2O_7)_2$ was performed within density functional theory (DFT) using the PBE0 exchange-correlation functional and a cc-pVDZ basis set. A corresponding optimization was also performed for the hypothetical monomer $ReO_2Cl(S_2O_7)$, thus allowing an estimation of the dimerization energy. The calculations were also used for assigning the Raman frequencies. Throughout the study, the Gaussian 03 program package was used,[23] and the vibrational frequencies were scaled by a factor of 0.96.[24]

Raman spectroscopy: Owing to the sensitivity of $ReO_2Cl(S_2O_7)$, the Raman spectrum (spectrometer FRA106, Bruker, Karlsruhe, Germany) was measured on a sample that was sealed together with a small amount of SO_3 in a glass tube. Important Raman intensities [cm^{-1}] (exptl./*calcd.*): 1434/*1450*, 1374/*1386*, 1209/*1216*, 1126/*1100*, 1065/*1068*, 1002/*1032*, 973/*1001*, 748/*751*, 658/*662*, 624/*625*, 588/*595*, 553/*550*, 530/*522*, 507/*510*, 473/*480*, 414/*398*, 407/*389*, 256/*282*.

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