Synthesis and Structure of SO_2 Bridged Trinuclear Re Cluster $(Et_4N)[Re_3(\mu_3\text{-}S)(\mu\text{-}SO_2)(\mu\text{-}S)_2Cl_6(PEt_3)_3]$

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A SO_2 bridged triangular rhenium cluster $(Et_4N)[Re_3(\mu_3\text{-}S)(\mu\text{-}SO_2)(\mu\text{-}S)_2Cl_6(PEt_3)_3]$ was isolated as one of the products in the reaction of $Re_3S_7Cl_7$ with triethylphosphine at room temperature. The $Re_3(\mu_3\text{-}S)(\mu\text{-}SO_2)(\mu\text{-}S)_2{}^{5+}$ cluster core is unique and differs in many points from that of closely related $Re_3(\mu_3\text{-}S)(\mu\text{-}S)_3{}^{5+}$ cluster.

Last years have been witnessing a remarkable progress in the chemistry of rhenium-sulfur clusters. Octahedral $Re_6(\mu_3\text{-}S)_8$[1] and tetrahedral $Re_4(\mu_3\text{-}S)_4$[2,6] clusters can easily be made now in a few steps starting from elements. In a recent series of papers, the reactions of triangular $[Re_3(\mu_3\text{-}S)(\mu\text{-}S_2)_3X_6]X$ (X=Cl, Br)[10,11] with PEt_3 were used to prepare a monocapped 8e cluster $[Re_3(\mu_3\text{-}S)(\mu\text{-}S)_3Cl_6(PEt_3)_3]^-$,[3] bicapped 9e $[Re_3(\mu_3\text{-}S)_2(\mu\text{-}S)_2(\mu\text{-}Cl)_2Cl_3(PEt_3)_3]$ and a 10e cluster $[Re_3(\mu_3\text{-}S)_2(\mu\text{-}S)_2(\mu\text{-}Br)_2Br_2(PEt_3)_4]$.[4] It thus appeared that by subtle changes in reaction conditions, other Re/S clusters may result in the $Re_3S_7Cl_7/PR_3$ systems. With this point of view the present study was undertaken.

$Re_3S_7Cl_7$ (0.3 g) was treated with PEt_3 (2 cm^3 20% w/w toluene solution) in benzene at room temperature under nitrogen atmosphere for 1 week. The solution was then filtered and dried. The solid was washed with Et_2O and redissolved in CH_2Cl_2, to which 1 g of Et_4NCl was added. The solution was left standing for 24 h, the solvent was removed in vacuum, the solid was washed with EtOH and extracted with hot acetone. The dark-brown solution was left standing for 4 weeks at room temperature and large black crystals formed. The elemental analysis for C,H,N,S,Cl agreed with the formula $(Et_4N)[Re_3(\mu_3\text{-}S)(\mu\text{-}SO_2)(\mu\text{-}S)_2Cl_6(PEt_3)_3]\cdot 2Me_2CO$ (**1**).[13] The IR spectrum (KBr) : 1200 cm^{-1} (S=O).

The structure of **1** was determined by single crystal X-ray analysis.[14] The view of the cluster anion (**1a**) and main interatomic distances are shown in Figure 1. The Re atoms form a monocapped triangle and are bridged by two S and one SO_2 ligands. The Re-Re distances are significantly longer (av. 2.81Å) than in any of previously observed triangular Re/S clusters, and the shortest one is bridged by SO_2 (2.79Å). In the closest structural analog of **1a**, $[Re_3(\mu_3\text{-}S)(\mu\text{-}S)_3Cl_6(PEt_3)_3]^-$, they are 2.72-2.73Å.[3] Another examples of SO_2 bridged Re-Re bonds are found in binuclear $[Re_2(SO_2)_2(CN)_8]^{6-}$ (2.636Å)[5] and rhombic $[Re_4(\mu_3\text{-}S)_2(\mu\text{-}SO_2)_4(CN)_{10}]^{8-}$ (2.837(1)Å).[6] Another feature is the very short distances between Re and S2, S3 atoms. With 2.24-2.26Å they are considerably shorter than in other compounds having Re-S-Re bridges (average value is about 2.30Å) and may reflect a bond order significantly higher than 1. Accordingly, the Re-S-Re angles are about 5° more obtuse at μ_2-S ligands in **1a** than in $[Re_3(\mu_3\text{-}S)(\mu\text{-}S)_3Cl_6(PEt_3)_3]^-$. The only other example of even shorter $Re\text{-}S_{(br.)}$ distances is found in $[(Re_2(\mu\text{-}S)(S_2CN^iBu_2)_4)_2(\mu\text{-}S_4)]PF_6$ (2.20-2.23Å).[12] The Re-μ_3-S and Re-SO_2 distances, on the other hand are within their usual limits. Thus the incomplete cubane framework Re_3S_4 has a high degree of distortion in **1a**.

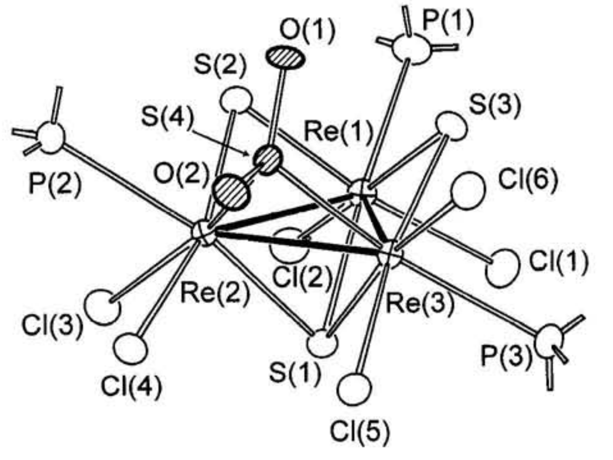

Figure 1. ORTEP drawing of the cluster anion in **1**. Ethyl groups are omitted for clarity. Selected interatomic distances and angles are: Re1-Re2 2.8075 (9), Re1-Re3 2.8209(6), Re2-Re3 2.7905 (5), Re-S1 2.349 (av.), Re1-S2 2.242(3), Re2-S2 2.241 (3), Re1-S3 2.268 (3), Re3-S3 2.244 (3), Re3-S4 2.362 (3), Re2-S4 2.362 (3), S(4)-O 1.475 (av.), Re3-Cl6 2.482 (3), Re-Cl (cis to μ_3-S) 2.422 (av.), Re-P 2.540Å (av.); O1-S4-O2 113.8 (4), Re1-S2-Re2 77.54 (9), Re1-S3-Re3 77.38 (9), Re2-S4-Re3 72.43 (8)°.

The S=O distance (1.47Å) is slightly shorter than those found in both above mentioned rhenium clusters with bridging SO_2 (1.49Å). An interesting feature is that unlike in $[Re_3(\mu_3\text{-}S)(\mu\text{-}S)_3Cl_6(PEt_3)_3]^-$,[3] in **1a** only two of three PEt_3 ligands are found in the positions trans to the capping sulfur, and the third phosphine ligand is cis to μ_3-S and trans to μ-SO_2 . This is not, however, reflected on the Re-P distances. On the other hand, the only Cl trans to μ_3-S possesses longer Re-Cl distance than the other five cis located chlorine atoms. Otherwise, the geometries within the PEt_3 ligands, the Et_4N cation and solvent acetone molecules are unexceptional.

If we assume the SO_2 ligand acting as 4e donor $SO_2{}^{2-}$, the connection between the cluster cores in **1a** and in $[Re_3(\mu_3\text{-}S)(\mu\text{-}S)_3Cl_6(PEt_3)_3]^-$ becomes immediately apparent. Both have Re in an average oxidation state 4.33. However this would require OSO angle close to 109° while the observed value is 113.8°. On the other hand, neutral 2e donor SO_2 would have the OSO angle 120°. It seems that the situation in **1a** is an intermediate between the two extreme cases. Though S=O vibrations in IR spectrum are strongly obscured by the vibrations of the organic parts of the complex, a band at 1200 cm^{-1} can be definitely assigned to S=O vibration and falls within the range characteristic for bridging SO_2.[17] The cluster $[Re_3(\mu_3\text{-}S)(\mu\text{-}S)_3Cl_6(PEt_3)_3]^-$ may form first and then be oxidized by oxygen to give **1a**. The oxygen may have come from leaking in a long period of storing. We have not succeeded in devising a more controllable and straightforward synthetic approach to **1** but the synthesis is reproducible on the scale indicated above. We have also found it expedient to expose the acetone solution to air for about 5 min. before final crystallization. The formation of SO_2 bridged clusters in $M/S/CN/O_2$ (M = Mo, Re) systems is well documented.[5,6,8] In the electron-rich 8e cluster $[Re_3(\mu_3\text{-}S)(\mu\text{-}S)_3Cl_6(PEt_3)_3]^-$ the two extra electrons in the $Re_3S_4^{5+}$ core are delocalized over $Re_3(\mu\text{-}S)_3$ ring, given the closeness of energy of Re 5d and S 3p AOs and the results of MO calculations for analogously built incomplete $Mo_3S_4^{4+}$ cubes.[9] This delocalization enhances negative partial charge on the bridging sulfur atoms and facilitates attack by an electrophilic agent (O_2) to give SO_2.

The preparation of the title compound is of particular interest not only because it allows us to follow changes in the cluster core geometry when only one of the bridging atoms in the core is modified (oxidized in this case) but also because it indicates possible existence of large family of clusters, related to the well-known incomplete cubes M_3S_4, and shows that , instead of S^{2-}, other more complex ligands can be accommodated.

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References and Notes

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14 crystal data for $(Et_4N)[Re_3(\mu_3\text{-}S)(\mu\text{-}SO_2)(\mu\text{-}S)_2Cl_6(PEt_3)_3]\cdot 2Me_2CO$: formula $C_{32}H_{77}NRe_3S_4Cl_6P_3O_4$, f_w 1532.46, space group $P2_1/c$, a= 22.14(2)Å, b=13.12(1)Å, c= 19.770(6)Å, β= 116.46(5)°, V= 5142(7) Å^3, Z=4, D_{calcd}= 1.979 g/cm^3, R= 0.039, R_w= 0.043 for 7086 observed reflections ($|F_o|>2\sigma|F_o|$; $5° < 2\theta < 59.8°$). The intensity data were collected with a Rigaku AFC7R diffractometer with MoKα (λ= 0.71069Å) radiation at 173K and corrected for Lorentz polarization and absorption (DIFABS). The structure was solved by direct methods (SIR92)[15] and non-hydrogen atoms refined anisotropically using full-matrix least-squares refinement.[16] Hydrogen atoms were not included in the refinement.
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