Synthesis of Trinuclear Rhenium Halide Sulfide Cluster Complexes with Triethylphosphine Ligands [$Re_3(\mu_3\text{-}S)_2(\mu_2\text{-}S)_2(\mu_2\text{-}Br)Br_2(PEt_3)_4$] and [$Re_3(\mu_3\text{-}S)_2(\mu_2\text{-}S)_2(\mu_2\text{-}Cl)Cl_3(PEt_3)_3$]

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The reactions of [$Re_3S_7X_6$]X (X = Br, Cl) with triethylphosphine formed a 10 electron cluster complex [$Re_3(\mu_3\text{-}S)_2(\mu_2\text{-}S)_2(\mu_2\text{-}Br)Br_2(PEt_3)_4$] or a 9 electron cluster complex [$Re_3(\mu_3\text{-}S)_2(\mu_2\text{-}S)_2(\mu_2\text{-}Cl)Cl_3(PEt_3)_3$].

Trinuclear metal cluster complexes have the basic importance for the study of the structure-MCE (metal cluster electron) relationships and also for the preparation of larger polyhedral cluster compounds using them as the building blocks.[1] The molybdenum and tungsten cluster complexes with π-donor ligands have been most extensively studied.[2] Trinuclear rhenium cluster compounds with chalcogenide and halide mixed ligands are still very rare and only a few examples are known. The first compound of this sort is [$Re_3S_7Cl_6$]Cl which has been reported by Timoshchenko et al.[3] The triangular cluster core is face-capped by a sulfur atom and the three edges are bridged by S_2 ligands. Each rhenium has two terminal chlorine ligands and there is an extra chlorine as a counter anion. The formal oxidation state of rhenium atoms is Re(V) and the compound has six metal cluster electrons. The structure is similar to that of $Mo_3S_7Cl_4$ which is a six-electron solid state chain compound with chlorine bridging.[4] There are a number of six-electron trinuclear cluster chalcogenide halide complexes of Mo(IV).[5-7] The present study has been undertaken with the view to synthesizing triethylphosphine derivatives starting from [$Re_3S_7X_6$]X (X = Br, Cl).

[$Re_3S_7Br_6$]Br was treated with a toluene solution (20 w/w %) of PEt_3 in benzene at room temperature under nitrogen atmosphere for 5 days. The solution was filtered and dried. The residue was washed with diethyl ether and extracted with THF. The solution was left standing for 24 h and black crystals formed. The elemental analysis agreed with the formula [$Re_3S_4Br_3(PEt_3)_4$] **1**. UV-Vis spectrum (CH_2Cl_2 solution; nm ($M^{-1}cm^{-1}$)):400 (sh), 470 (sh), 620 (1.2×10^3), 890 (5.4×10^2), 1100 (5.9×10^2), 1620 (5.2×10^2).

The structure of **1** was determined by the single-crystal X-ray analysis.[8] The ORTEP drawing and the selected interatomic distances are shown in Figure 1. The cluster core is a triangle of rhenium atoms capped by two sulfur atoms and bridged by two sulfur and a bromine atoms. There are two terminal bromine and four triethylphosphine ligands coordinated to the rhenium atoms. The Re-Re distances range from 2.648 Å to 2.687 Å and the Re_3 is an isosceles triangle with the shorter edge bridged by a bromine atom. The Re-Re-Re angles are 59.11 - 60.54 °.

[$Re_3S_7Cl_6$]Cl was reacted in a similar manner to the preparation of **1** and the product was crystallized from acetone to give dark brown crystals in 26% yield. The elemental analysis agreed with the formula [$Re_3S_4Cl_4(PEt_3)_3$] **2**. UV-Vis spectrum (CH_2Cl_2 solution; nm ($M^{-1}cm^{-1}$)): 380 (sh), 430 (sh), 500 (sh), 610 (sh), 800 (sh), 1050 (3.7×10^2), 1570 (2.5×10^2). A $^{31}P\{^1H\}$ NMR spectrum of a CD_2Cl_2 solution (85% H_3PO_4 external reference) shows resonances at -0.34, -4.72, and -4.84 ppm.

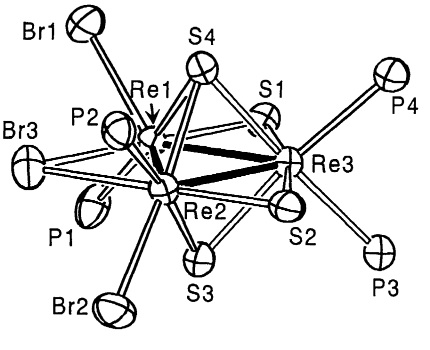

Figure 1. ORTEP drawing of [$Re_3S_4Br_3(PEt_3)_4$]. Ethyl groups are omitted for clarity. Mean interatomic distances are: Re - Re 2.672; Re - Br 2.576; Re - μ_2-Br 2.634; Re - μ_2-S 2.338; Re - μ_3-S 2.369; Re - P 2.482 Å.

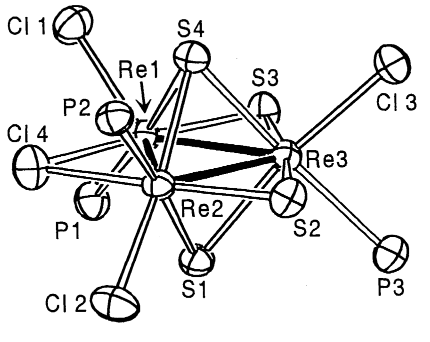

Figure 2. ORTEP drawing of [$Re_3S_4Cl_4(PEt_3)_3$]. Ethyl groups are omitted for clarity. Mean interatomic distances are: Re - Re 2.653; Re - Cl 2.399; Re - μ_2-Cl 2.416; Re - μ_2-S 2.346; Re - μ_3-S 2.380; Re - P 2.505 Å.

The ORTEP drawing of the structure of **2** determined by the single-crystal X-ray analysis[9] and the selected distances are illustrated in Figure 2. The cluster core is similar to that of **1** consisting of three rhenium atoms with two capping sulfur, two bridging sulfur and a bridging chlorine atoms. The Re-Re distances are 2.628 - 2.677 Å and the Re1 - Re2 which has a bridging chlorine is the longest one. Each rhenium atom is coordinated by a terminal chlorine and a triethylphosphine ligands. The triethylphosphine ligands coordinated to Re1 and Re3 and that coordinated to Re2 are on the opposite sides of the Re_3 face. Although the distinction of sulfur and chlorine atoms by the X-ray crystallography is difficult, the structure of the bromide derivative **1** suggests that both of the face-capping atoms in the chloride derivative **2** are also sulfur atoms because the starting compounds $[Re_3S_7X_6]X$ (X = Br, Cl) are analogous and the reaction conditions are similar. Other circumstantial evidence comes from the average distance between the rhenium and bridging sulfur atoms (2.35 Å) which is ca. 0.07 Å shorter than that between the rhenium and bridging chlorine atoms (2.42 Å). There are some reported examples of the distinction of sulfur and chlorine atoms by the X-ray crystallography of cluster complexes.[10,11] The ^{31}P NMR spectrum with three separate resonances is also consistent with the chiral structure. The compound has no optical activity and is probably racemic.

The complex **2** has nine metal cluster electrons with three Re(IV) centers in contrast with the complex **1** which has ten metal cluster electrons. The exact reason why the bromide derivative has an extra triethylphosphine instead of a terminal halogen is not clear at present. This should be related to a combination of electronic and steric effects of a halogen and triethylphosphine to displace a terminal bromo ligand by triethylphosphine more readily than a terminal chloro ligand. The displacement results in one-electron reduction of the cluster complex.

We have reported the synthesis of a triangular molybdenum cluster complex $[Mo_3(\mu_3\text{-}S)(\mu_2\text{-}S)_3(PMe_3)_6]$ with eight metal cluster electrons.[12] The HOMO calculated for a model complex $[Mo_3S_5(PH_3)_6]$ is the non-degenerate a_1'' orbital and lack of distortion in the real complex (equilateral triangular geometry) has been explained from the standpoint of the occupation of the a_1'' by two electrons. The present rhenium cluster complexes have also two face-capping sulfur and edge-bridging sulfur and halogen ligands but have lower symmetries (isosceles triangular geometries). As only six metal cluster electrons are necessary for the three M-M bonds in the triangular clusters, excessive electrons can lead to the weakening of the metal-metal bonds. The 10 e^- cluster **1** has longer Re-Re distances than those in the 9 e^- cluster **2**. However, the Re-Re distances in both of the cluster complexes are shorter than the Mo-Mo distance 2.714 Å in the 6 e^- cluster. As the rhenium clusters have more electrons than the molybdenum cluster, the shorter Re-Re distances cannot be explained by the simple argument of the relationship between the M-M distance and the number of MCE. It is to be noted that the Re-Re distances 2.689 Å and 2.702 Å in the starting compounds $Re_3S_7Br_7$ and $Re_3S_7Cl_7$ (10 e^-),[3] respectively, are also shorter than the Mo-Mo distance 2.745 Å in $Mo_3S_7Cl_4$ (6 e^-).[4]

References and Notes

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8 Crystal data for $[Re_3S_4Br_3(PEt_3)_4].CH_2Cl_2$: formula $C_{25}H_{62}Br_3Cl_2P_4Re_3S_4$, fw 1484.1, space group $P2_12_12_1$, a = 13.327(2) Å, b = 32.257(3) Å, c = 11.313(2) Å, V = 4863(1) Å^3, Z = 4, D_{calcd} = 2.027 g cm^{-3}, R = 0.055, R_w = 0.060 for 5198 observed reflections ($|F_o| > 3\sigma(|F_o|)$; $6° < 2\theta < 55°$). The intensity data were collected by a Rigaku AFC-5R diffractometer with MoKα (λ = 0.7107 Å) radiation at 294 K. The structure was solved by the teXsan package programs.[13] The positions of non-hydrogen atoms were located by the direct methods and on Fourier maps. The full-matrix refinements were performed with the ANYBLK program.[14] The Re, Br, and P atoms were refined anisotropically, and other atoms isotropically. Hydrogen atoms were not included in the refinements.

9 Crystal data for $[Re_3S_4Cl_4(PEt_3)_3]$: formula $C_{18}H_{45}Cl_4$-$P_3Re_3S_4$, fw 1183.2, space group $P2_1$, a = 11.230(4) Å, b = 11.861(3) Å, c = 13.165(4) Å, β = 106.88(2) °, V = 1678.0(9) Å^3, Z = 2, D_{calcd} = 2.342 g cm^{-3}, R = 0.035, R_w = 0.028 for 8927 observed reflections ($|F_o| > 3\sigma(|F_o|)$; $6° < 2\theta < 60°$). The intensity data were collected by a Rigaku AFC-7R diffractometer with MoKα (λ = 0.7107 Å) radiation at 297 K. The structure was solved by the similar procedure described for the compound **1**.

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