Synthesis of a Mixed-Metal Cluster Complex of Rhenium and Nickel [$Re_3NiS_4Cl_6(PEt_3)_4$]

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Condensation of [$Ni(cod)_2$] with a trinuclear rhenium chloro sulfido cluster complex prepared from [$Re_3S_7Cl_6$]Cl and triethylphosphine forms a mixed metal cluster complex [$Re_3NiS_4Cl_6(PEt_3)_4$]. The cluster complex has 17 metal cluster electrons and is paramagnetic. The four metal atoms form a cubane structure with face-capping sulfur atoms.

Chemistry of rhenium cluster compounds is much less explored[1] than the group 6 metal cluster chemistry.[2-5] This is in part due to the lack of convenient solid state cluster compounds which can be utilized as the starting materials. Rhenium is a group 7 element and has one more d electron than molybdenum or tungsten. Preparation of the cluster compounds which are similar electronically and structurally to those of the group 6 metals requires the oxidation of rhenium to decrease the number of metal cluster electrons. In the case of mixed chalcogenide halide cluster compounds, the change of halogens (1-) into chalcogens (2-) or the change of neutral ligands (0) into halide ligands (1-) or the oxidation of the cluster core by the presence of outer-sphere counter anions are used to adjust the oxidation states. This depends on the availability of the coordination sites because the coordination number and geometry around rhenium are considered to be similar to those of molybdenum or tungsten. For example, a molybdenum atom can be replaced by a rhenium atom by changing a halogen into a sulfur atom keeping the number of valence electrons identical. The synthesis of a series of octahedral rhenium cluster compounds with 24 metal cluster electrons has exemplified the effective application of this isoelectronic concept to prepare the rhenium analogues of the Chevrel type cluster compounds.[6]

Recently, the first trinuclear rhenium chalcogenido halo cluster compounds [$Re_3E_7X_6$]X[7,8] and some derivatives have been reported.[9] These ionic cluster compounds have the trinuclear cluster cores with a capping chalcogen and three bridging E_2 ligands which are similar to the molybdenum cluster compounds $Mo_3E_7X_4$ but with three more halogens to keep the number of the metal cluster electrons six. Treatment of the solid state compounds with triethylphosphine gives mono-capped and bi-capped trinuclear rhenium cluster complexes coordinated by triethylphosphine ligands.[10,11] The present communication describes the formation of a tetranuclear mixed metal cluster complex when a trinuclear rhenium cluster complex is condensed with [$Ni(cod)_2$].

[$Re_3S_7Cl_6$]Cl in benzene was reacted with a solution of PEt_3 (20 w/w % in toluene) at room temperature for 3 days. The dark red solution was filtered and dried under reduced pressure. The residue was washed with diethyl ether and dissolved in benzene. A solution of [$Ni(cod)_2$] (cod = cycloocta-1, 5-diene) in THF was added to the benzene solution. After 1 day the solvents were removed under reduced pressure and the residue was extracted with THF. Benzene and ethanol were layered on the THF solution which was left standing for 2 weeks to give black crystals in 16% yield. The elemental analysis agreed with the formula [$Re_3NiS_4Cl_6(PEt_3)_4$].THF **1**.[12]

The structure of **1** was determined by the single-crystal X-ray analysis.[13] The ORTEP drawing and the selected bond distances are shown in Figure 1. Three rhenium and a nickel atoms are located on the apices of the metal cubane and a μ_3-sulfur atom caps each face. Each rhenium is coordinated by a triethylphosphine and two chlorine ligands whereas nickel is coordinated by a triethylphosphine. The coordination around the rhenium atoms is octahedral and that of the nickel atom tetrahedral if the metal-metal bondings are neglected. The average Re-Re distance is 2.806 Å and the average Re-Ni distance 2.710 Å. The average Re-Ni-Re angle is 62.3°. The number of metal cluster electrons is 17 and the compound should be paramagnetic as supported by the ^1H and ^{31}P NMR spectra which did not show any significant peaks in normal regions.

The present mixed metal cluster complex is similar to [$Mo_3NiS_4(H_2O)_{10}$]$^{4+}$ complexes reported by Shibahara et al.[14] These Mo_3Ni systems have 16 metal cluster electrons and diamagnetic. The mean Mo-Mo distance is 2.755 Å and the mean Mo-Ni distance is 2.640 Å. The metal-metal distances in the

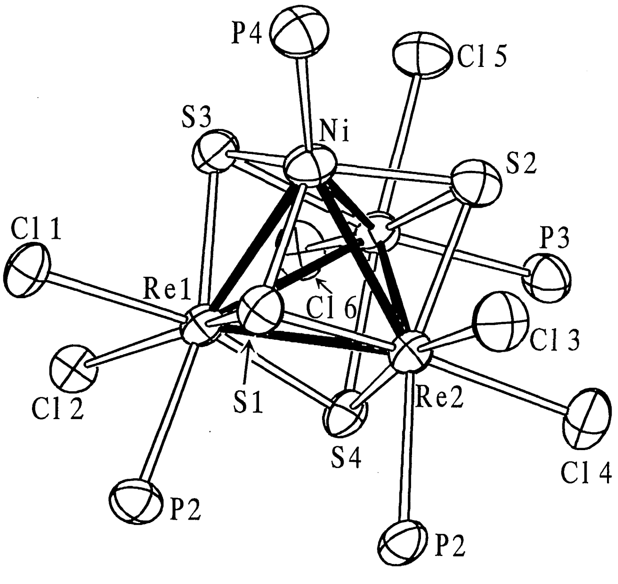

Figure 1. ORTEP drawing and mean bond distances (Å) for **1**. Ethyl groups are omitted for clarity. Re-Re 2.806, Re-Ni 2.710, Re-S 2.319, Ni-S 2.193, Re-P 2.571, Ni-P 2.173, Re-Cl 2.441.

Re_3Ni cluster are about 0.05 Å longer than those in the Mo_3Ni clusters, reflecting that the extra metal cluster electrons over 12 (corresponding to 6 metal-metal bonds in a cubane cluster) should enter either metal-metal non-bonding or anti-bonding orbitals. The single bond covalent radius of rhenium is 2.57 Å and smaller than 2.62 Å for molybdenum.[15] The elongation of the Re-Re and Re-Ni distances as compared with the Mo-Mo and Mo-Ni distances is therefore pronounced. The larger electrostatic repulsion due to the higher positive charges on the rhenium atoms may also be responsible for the longer metal-metal distances.

The $[Re_3(\mu_3\text{-}S)(\mu_2\text{-}S)_3Cl_6(PEt_3)_3]^+$ cluster cation which is formed by the reaction of $[Re_3S_7Cl_6]Cl$ with triethylphosphine consists of three Re^{5+} centers and has 6 metal cluster electrons. The capture of a nickel atom and one electron reduction forms the present mixed valent cluster complex with two Re^{5+} and a Re^{4+} ions. There are many mixed metal cluster complexes based on the 6 electron incomplete cubane clusters of molybdenum and tungsten,[2,3,16,17] and the synthesis of the present mixed metal cluster of rhenium and nickel will unveil the similar mixed metal cluster chemistry based on the trinuclear rhenium cluster complexes.

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12 Found: C, 23.71; H, 4.70; Calcd for $C_{28}H_{68}Cl_6NiOP_4\text{-}Re_3S_4$: C, 22.38; H, 4.56%.
13 Crystal data for $[Re_3NiS_4Cl_6(PEt_3)_4]$.THF: formula $C_{28}H_{68}Cl_6NiOP_4Re_3S_4$, fw = 1503.0, space group $P2_1/a$, a = 15.407(4) Å, b = 17.597(5) Å, c = 18.069(4) Å, β = 99.67(2)°, V = 4829(2) Å^3, Z = 4, D_{calcd} = 2.067 g/cm^3, R = 0.054, R_w = 0.039 for 6503 observed reflections ($|F_o| > 4\sigma(|F_o|)$; $6° < 2\theta < 60°$). The intensity data were collected by a Rigaku AFC7R diffractometer with MoKα (λ = 0.71069 Å) radiation at 291 K. In the crystal structure determination, the positions of the rhenium and nickel were determined by Patterson method,[18] and other non-hydrogen atoms were located on Fourier maps. The full-matrix refinements were performed with the texSan programs.[19] The non-hydrogen atoms except for those of the solvent molecule were refined anisotropically. Hydrogen atoms were not included in the refinements.
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