

The Synthesis and MALDI-MS Characterization of New Ruthenium Sulfide Clusters

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Study of metal sulfide clusters pertains to biological and industrial catalysts. The active sites of many metalloenzymes contain metal clusters with inorganic sulfide groups as part of the cluster framework. These metalloenzymes catalyze the most fundamental reactions such as electron transfer and small molecule activation (H_2 , N_2 and CO).¹ Industrially, W and Mo sulfide materials promoted by Co and Ni are used as hydrotreatment catalysts.² Sulfides of the noble metals (Ru, Rh, Os, and Ir) have been shown to be much more active catalysts.³ Synthetic clusters have long been used as models for the binding and reactivity of substrates on surfaces of heterogeneous catalysts.⁴ Finally, the cluster-based Chevrel phases $M'Mo_6S_8$ exhibit particularly interesting magnetic, electronic, and catalytic properties.^{5,6} The synthesis of molecular Chevrel clusters is topical and has been the subject of extensive research for the past two decades; four general methods have been developed: (1) substitution of S for X in the metal halide (M_6X_{12})⁷ (2) excision of Mo_6S_8 clusters from the bulk phase by molten cyanide⁸ (3) reductive dimerization of M_3S_4 clusters⁹ (4) condensation of metal monomers with sulfide.^{10,11} The logical synthesis of these two concepts, the high activities of Ru-S materials and clusters, suggests ruthenium sulfide clusters as catalysts or catalyst precursors.

The reaction of Ru(II) coordination complexes ($RuCl_2(DMSO)_4$, $RuCl_2(PPh_3)_3$) with S^{2-} sources ($S(tms)_2$, $NaSH$) results in the formation of three main clusters with core formulas $Ru_4S_6(PPh_3)_4$, $Ru_5S_6(PPh_3)_5$, and the first ruthenium sulfide Chevrel cluster $Ru_6S_8(PPh_3)_6$ (Figure 1). MALDI-MS (Matrix Assisted Laser Desorption/Ionization Mass Spectroscopy) was found to work well as an analytical technique for identifying the products. MALDI-MS was the principal means used to assay reaction mixtures and purity of product, which facilitated the development of reliable synthetic and purification procedures for the three compounds (Figure 2).

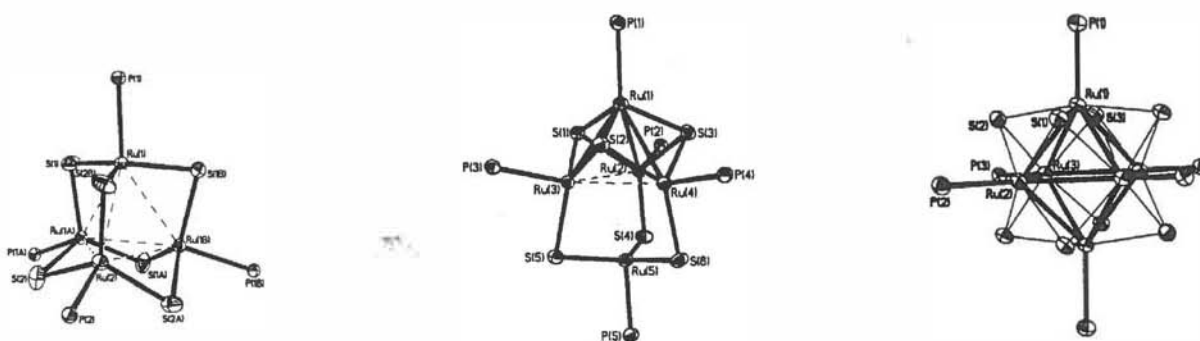


Figure 1. Thermal ellipsoid plots of $Ru_4S_6(PPh_3)_4$, $Ru_5S_6(PPh_3)_5$, and $Ru_6S_8(PPh_3)_6$ drawn at 35%. Carbon and hydrogen atoms have been omitted for clarity.

The structure of the $\text{Ru}_4\text{S}_6(\text{PPh}_3)_4$ cluster is highly symmetrical with a tetrahedron of Ru atoms with edge-bridging S atoms. This cluster type is unknown for Ru but is common among late transition metal thiolate clusters and post-transition metal sulfides (e.g., $[\text{Zn}_4(\text{SPh})_{10}]^{2-}$, $[\text{Ga}_4\text{S}_{10}]^{8-}$).¹² The only example of another such transition metal cluster is $\text{W}_4\text{S}_6(\text{PMe}_2\text{Ph})_4$.¹³ The four-coordinate geometry at each Ru center, discounting any Ru-Ru interactions (Ru-Ru = 2.93 Å), is also unusual. Reaction of this cluster with alkyl phosphines (PR_3 ; R = Me, Et, Bu), results in a range of substituted products, with the degree of substitution proportional to the basicity of the PR_3 ligand.

The Ru_5S_6 cluster core contains a $\{\text{Ru}_4\text{S}_3\}$ subunit with apparent Ru-Ru bonding (Ru-Ru = 2.79 Å), reminiscent of the $\{\text{Fe}_4\text{S}_3\}$ subunits in nitrogenase FeMo cofactor. Similar clusters with MFe_4S_6 (M = Mo, V) heterometallic cores have been synthesized.^{14,15} The fifth Ru is also four-coordinate, but is distant from the $\{\text{Ru}_4\text{S}_3\}$ subunit (Ru(5)-Ru_{eq} = 3.02 Å).

The first Ru Chevrel cluster has a highly symmetrical core consisting of an octahedron of Ru atoms with each face capped by a S atom. The Ru-Ru distances are approximately 2.80 Å suggesting a bonding interaction. The average oxidation state of the Ru atoms is +2.67; the oxidation of the starting material is presumed to occur via production of H_2 . A more soluble derivative was sought using $\text{Ru}_3\text{Cl}_8(\text{PEt}_3)_4$ and NaSH; $\text{Ru}_6\text{S}_8(\text{PEt}_3)_6$ was detected as the main product of the reaction mixture using MALDI-MS but could not be readily purified. Crystallographic characterization showed the core to be nearly identical to that of $\text{Ru}_6\text{S}_8(\text{PPh}_3)_6$.

The clusters $\text{Ru}_4\text{S}_6(\text{PPh}_3)_4$ and $\text{Ru}_5\text{S}_6(\text{PPh}_3)_5$ have rich electrochemistry, with three and four redox events, respectively, in the cyclic voltammograms. The electrochemistry of $\text{Ru}_6\text{S}_8(\text{PPh}_3)_6$ could not be thoroughly investigated due to its insoluble nature in pure crystallized form. The Fe analog has been characterized in four oxidation states; the Ru Chevrel is expected to be similarly electroactive.^{16,17}

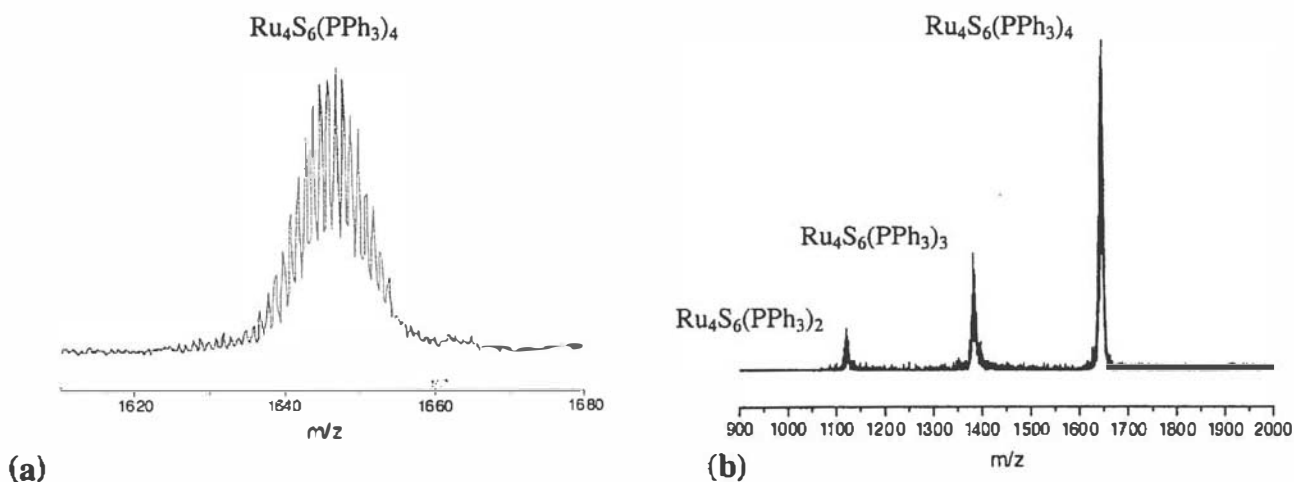


Figure 2. MALDI mass spectrum of $\text{Ru}_4\text{S}_6(\text{PPh}_3)_4$ showing (a) the resolution of the molecular ion peak envelope and (b) the consecutive loss of PPh_3 ligands.

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