

Tetrathiometallates in Synthesis and Catalysis

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Final Seminar

April 15, 2003

While sulfur is often described as a catalyst poison, most of the remarkable catalysts in industry¹ and in nature² feature metals embedded in a sulfur-rich coordination sphere. Transition metal sulfides are involved in a variety of applications which includes being used as secondary cathodes in Li-TiS₂ batteries³ and as catalysts for major petrochemical processes such as MoS₂ in hydrodesulfurization (HDS) catalysis.¹ A recent and popular theory of the origin of life invokes a key role played by Fe-S and Fe-Ni-S species.⁴ A special class of transition metal sulfides are the tetrathiometallates. They are molecular anions composed of a single metal atom surrounded by a shell of sulfur. This configuration is analogous to the metal sulfides used as catalysts in industry, but they are soluble which allows for a greater range of spectroscopic techniques for characterization.

Chemistry of ReS₄⁻

Rhenium sulfide materials are of interest, as ReS₂ is a one of the best HDS catalysts and Re₂S₇ is a widely used hydrogenation catalyst.⁵ The cyclic voltammogram (CV) of ReS₄⁻ (Figure 1) indicates a strange oxidation event-stripping peak couple separated by more than 1.4 V. When the working electrode (Pt) is held at 500 mV vs. Ag|AgCl in MeCN solutions of ReS₄⁻, a black compound is deposited upon the electrode. If the electrode is removed, washed, and inserted into fresh MeCN-electrolyte solution, ReS₄⁻ can be regenerated at a potential of -900 mV vs. Ag|AgCl. This black material can be produced in bulk by electrochemical methods and by chemical oxidants. Both of these products have a Re:S ratio of 1:4, as determined by X-ray energy dispersive spectroscopy. The material was determined to be amorphous by x-ray powder diffraction. Structural information for ReS₄ and Re₂S₇ was obtained by x-ray absorption spectroscopy. Re₂S₇, another amorphous phase of rhenium sulfide, was previously studied by Hibble et al.⁶ The new ReS₄ material was determined to be disordered with a composition between Re(S)₁(S₂)_{1.5} and Re(S)₂(S₂)₁. Possible structures include a Re₄ rhombohedron (Figure 2) similar to the structure proposed for Re₂S₇, and linear chains of ReS₄ units.⁷

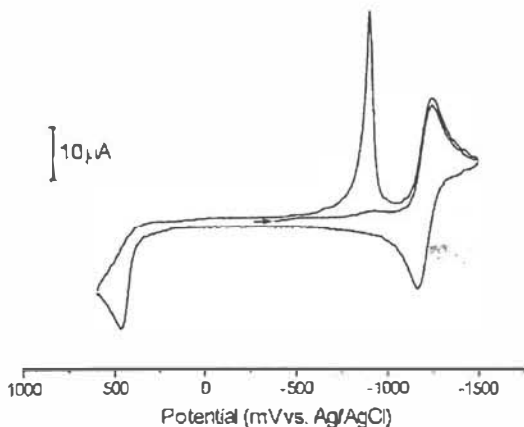


Figure 1. CV of Et₄N[ReS₄] in MeCN.

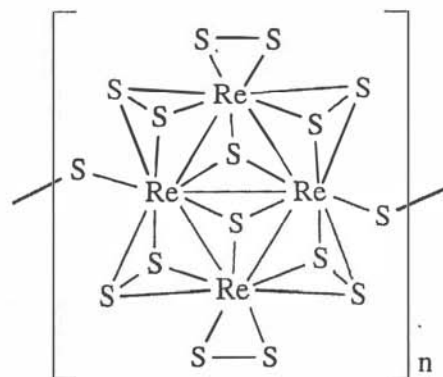
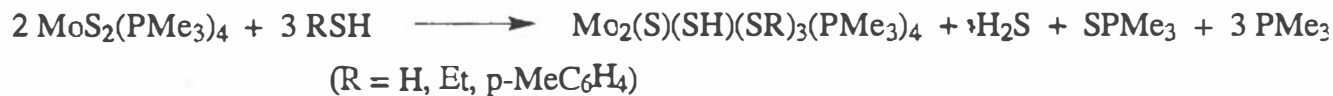


Figure 2. Possible Structure of ReS₄.

In HDS, sulfur removal from the catalyst creates vacant sites for catalysis to occur. In a similar fashion, we are interested in the chemistry that occurs when sulfur is removed from the tetrathiometalates. The reaction of $\text{Et}_4\text{N}[\text{ReS}_4]$ with PMe_3 , a sulfur abstraction agent and a good trapping ligand, was investigated. The resulting $\text{Et}_4\text{N}[\text{Re}_2\text{S}_4(\text{SH})(\text{PMe}_3)_3]$ complex was isolated after one month reaction time. The analogous reaction with one equiv of H_2S produced an immediate conversion to this complex. Further equivs of H_2S produced $\text{Re}(\text{SH})_2(\text{PMe}_3)_4$ and $\text{ReH}(\text{SH})_2(\text{PMe}_3)_2$.⁸ The interaction of these compounds with small molecules such as H_2 , D_2 , H_2S , and CO was explored. The compound $\text{ReH}(\text{SH})_2(\text{PMe}_3)_4$ demonstrated an interesting intramolecular exchange of the SH and the hydride which was studied by synthesizing $\text{ReD}(\text{SH})_2(\text{PMe}_3)_4$ through selective H/D exchange with D_2 at the hydridic position. The only other systems capable of this sort of intramolecular exchange are $\text{Ru}(\text{SH})(\text{H})(\text{CO})_2(\text{PPh}_3)_2$ and $\text{RuH}(\text{SH})(\text{PPh}_3)_3$,⁹ however, the hydrides on these species do not exchange with D_2 .

Chemistry of MoS_4^{2-}

In a set of reactions analogous to the aforementioned ReS_4^- chemistry, $(\text{NH}_4)_2[\text{MoS}_4]$ was reacted with PMe_3 and produced $\text{MoS}_2(\text{PMe}_3)_4$ in high yields.¹⁰ The previously known synthesis of this compound was multi-step and used very specialized reagents.¹¹ The species MoS_2L_4 ($\text{L} = \text{PR}_3, \text{SR}_2$), which are formal adducts of monomeric MoS_2 ,¹² are of interest because they could in principle oligomerize to afford polymetallic aggregates, which might exhibit new structural or catalytic properties. This is the case, as $\text{MoS}_2(\text{PMe}_3)_4$ reacts with RSH ($\text{R} = \text{H}, \text{Et}, \text{C}_6\text{H}_4\text{CH}_3$) to produce a family of dinuclear and tetranuclear compounds as shown in the equation below. The compounds range from the coordinatively and electronically unsaturated intermediate $\text{Mo}_2\text{S}_2(\text{SEt})_4(\text{PMe}_3)_2$, to $\text{Mo}_4\text{S}_6(\text{SH})_2(\text{PMe}_3)_6$ which has a core structure similar to MoS_2 .



The decomposition of H_2S is extremely industrially important. The method currently employed in much of industry is the Claus process which completely oxidizes H_2S to S_8 and H_2O in a very exothermic, stepwise reaction.¹³ A process capable of producing H_2 from H_2S would allow the hydrogen to be recycled back into the reactors, making the process much more economical. Unlike $(\text{NH}_4)_2[\text{MoS}_4]$, solutions of $(\text{Et}_4\text{N})_2[\text{MoS}_4]$ with PMe_3 are stable. If H_2S is added, the MoS_4^{2-} acts as a catalyst to produce H_2 and SPMe_3 with a turnover number (TON) of 25.3 in 2.5 h at 25 °C.¹⁰ This type of catalysis was previously observed for $\text{ReH}(\text{SH})_2(\text{PMe}_3)_4$, however, at a much slower rate (TON of 21.6 in 329 h).⁸

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