While sulfur is often described as a catalyst poison, most of the remarkable catalysts in industry and in nature 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 batteries and as catalysts for major petrochemical processes such as MoS2 in hydrodesulfurization (HDS) catalysis. A recent and popular theory of the origin of life invokes a key role played by Fe-S and Fe-Ni-S species. 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. 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. The new ReS4 material was determined to be disordered with a composition between Re(S8)(S2)n and Re(S6)(S2)n. Possible structures include a Re4 rhombohedron (Figure 2) similar to the structure proposed for Re2S7, and linear chains of ReS4 units.

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 tetrathiometallates. The reaction of \( \text{Et}_4\text{N}[\text{ReS}_4] \) with \( \text{PMe}_3 \), 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 \( \text{H}_2\text{S} \) produced an immediate conversion to this complex. Further equivs of \( \text{H}_2\text{S} \) produced \( \text{Re}(\text{SH})_2(\text{PMe}_3)_4 \) and \( \text{ReH}(\text{SH})_2(\text{PMe}_3)_4 \). The interaction of these compounds with small molecules such as \( \text{H}_2, \text{D}_2, \text{H}_2\text{S}, \) and \( \text{CO} \) was explored. The compound \( \text{Re}(\text{SH})_2(\text{PMe}_3)_4 \) demonstrated an interesting intramolecular exchange of the \( \text{SH} \) and the hydride which was studied by synthesizing \( \text{ReD}(\text{SH})_2(\text{PMe}_3)_4 \) through selective H/D exchange with \( \text{D}_2 \) 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 \( \text{RuH}(\text{SH})(\text{PPh}_3)_3 \), however, the hydrides on these species do not exchange with \( \text{D}_2 \)

Chemistry of \( \text{MoS}_2 \)

In a set of reactions analogous to the aforementioned \( \text{ReS}_4 \) chemistry, \( (\text{NH}_4)_2[\text{MoS}_4] \) was reacted with \( \text{PMe}_3 \) and produced \( \text{MoS}_2(\text{PMe}_3)_4 \) in high yields. The previously known synthesis of this compound was multi-step and used very specialized reagents. The species \( \text{MoS}_2\text{L}_4 \) (\( \text{L} = \text{PR}_3, \text{SR}_2 \)), which are formal adducts of monomeric \( \text{MoS}_2 \), are of interest because they could in principle oligomerize to afford polymeric 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 tetracene 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 \( \text{MoS}_2 \).

\[
2 \text{MoS}_2(\text{PMe}_3)_4 + 3 \text{RSH} \rightarrow \text{Mo}_2(\text{S})(\text{SH})(\text{SR})_3(\text{PMe}_3)_4 + \text{H}_2\text{S} + \text{SPMe}_3 + 3 \text{PMe}_3 \quad (\text{R} = \text{H}, \text{Et}, \text{p-MeC}_6\text{H}_4) 
\]

The decomposition of \( \text{H}_2\text{S} \) is extremely industrially important. The method currently employed in much of industry is the Claus process which completely oxidizes \( \text{H}_2\text{S} \) to \( \text{S}_8 \) and \( \text{H}_2\text{O} \) in a very exothermic, stepwise reaction. A process capable of producing \( \text{H}_2 \) from \( \text{H}_2\text{S} \) 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 \( \text{PMe}_3 \) are stable. If \( \text{H}_2\text{S} \) is added, the \( \text{MoS}_4 \) acts as a catalyst to produce \( \text{H}_2 \) and \( \text{SPMe}_3 \) with a turnover number (TON) of 25.3 in 2.5 h at 25 °C. 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).

References


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