

Synthesis Of Transition Metal Polysulfide Complexes From Metal Powders

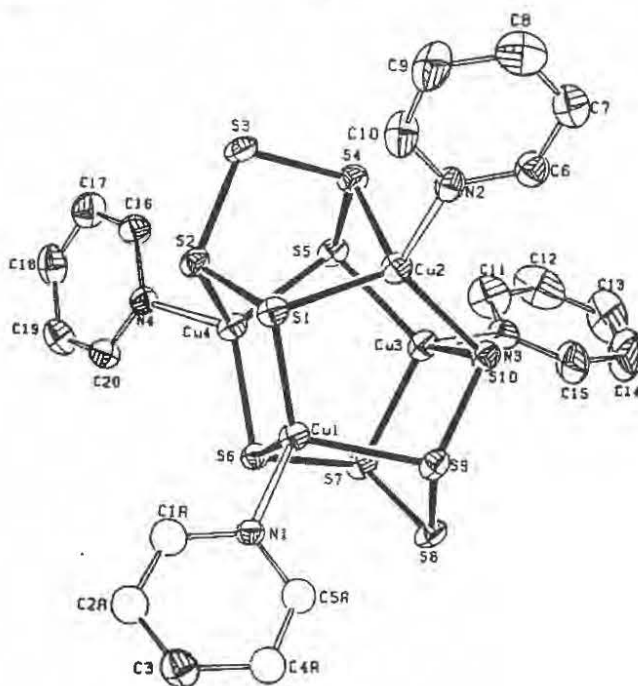
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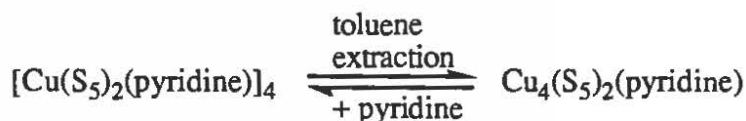
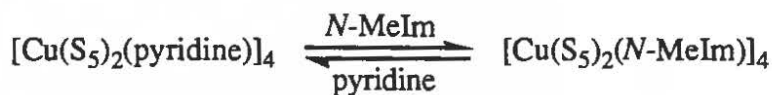
Covellite, $\text{Cu}^{\text{I}}_2(\text{S}_2)\text{Cu}^{\text{II}}\text{S}$, and $\text{YBa}_2\text{Cu}^{\text{II}}_2\text{Cu}^{\text{III}}\text{O}_{7-x}$ are similar in that both are superconductors containing layered structures and mixed valent copper centers [1,2]. The former has a critical temperature (T_c) of 1.66 K, while the latter has a T_c of 92 K. Our studies on $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ focused on ^{17}O -labelling of samples of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ and the ^{17}O NMR studies of these samples [3]. Our work on covellite began with studies of its synthesis at low temperatures. This work led to the discovery of a low temperature route to metal sulfides.

We initially prepared covellite by the reaction of a suspension of copper metal and elemental sulfur in refluxing pyridine. When the same reaction was conducted at room temperature we obtained amorphous CuS and a soluble species. Chemical, spectroscopic and structural studies showed that the soluble species was $[\text{Cu}(\text{S}_5)_2(\text{pyridine})]_4$ [4].

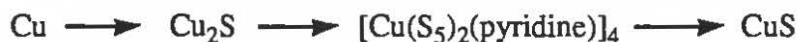


Subsequently it was found that the reaction between copper and sulfur is particularly rapid in *N*-methylimidazole (*N*-MeIm), affording $[\text{Cu}(\text{S}_5)_2(\text{N-MeIm})]_4$ in 50% yield.

$[\text{Cu}(\text{S}_5)_2(\text{pyridine})]_4$ was shown to undergo ligand substitution and ligand removal reactions at room temperature:



At 70 °C, the cluster converts to covellite. Covellite can also be prepared at room temperature by reacting $[\text{Cu}(\text{S}_5)_2(\text{pyridine})]_4$ with copper metal. Furthermore it was found that the cluster formed from Cu_2S . Collectively these results suggest the following sequence of events for the conversion of Cu to CuS :



This study thus provided mechanistic insight into the formation of metal sulfides from their elements.

Other first row transition metals which react with $\text{S}_8/\text{N-MeIm}$ at room temperature include manganese, iron and nickel [5]. The product in all of these cases is $[\text{M}(\text{N-MeIm})_6]\text{S}_8$ ($\text{M} = \text{Mn, Fe, Ni}$). Structural analysis of $[\text{M}(\text{N-MeIm})_6]\text{S}_8$ provides the first evidence for S_8^{2-} anion, the product of the $2e^-$ reduction of S_8 . Magnetic susceptibility studies revealed that the Mn and Ni salts show a Curie behavior, while the Fe salt shows a Curie-Weiss behavior. UV/visible spectroscopy showed that the S_8^{2-} anion dissociates to S_x^- species in solution. A preliminary study on the reactivity of $[\text{Mn}(\text{N-MeIm})_6]\text{S}_8$ showed that it can be converted to $[\text{Mn}(\text{N-MeIm})_6][\text{Mn}(\text{S}_5)(\text{S}_6)]$, which showed similar spectroscopic properties to $(\text{PPh}_4)_2-[\text{Mn}(\text{S}_5)(\text{S}_6)]$.

Zinc metal reacts with $\text{S}_8/\text{N-MeIm}$ at 90 °C to form $[\text{ZnS}(\text{N-MeIm})]_n$ when $\text{Zn} : \text{S} = 1 : 1$ and $\text{ZnS}_6(\text{N-MeIm})_2$ [6] when $\text{Zn} : \text{S} = 1 : 6$. The two compounds are interconvertible via addition of elemental sulfur or zinc. $\text{ZnS}_6(\text{N-MeIm})_2$ was shown to react with $(\text{MeCp})_2\text{TiCl}_2$ to form $(\text{MeCp})_2\text{TiS}_5$, and with $(\text{PPh}_4)_2\text{S}_6$ to form $(\text{PPh}_4)_2[\text{Zn}(\text{S}_6)_2]$.

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