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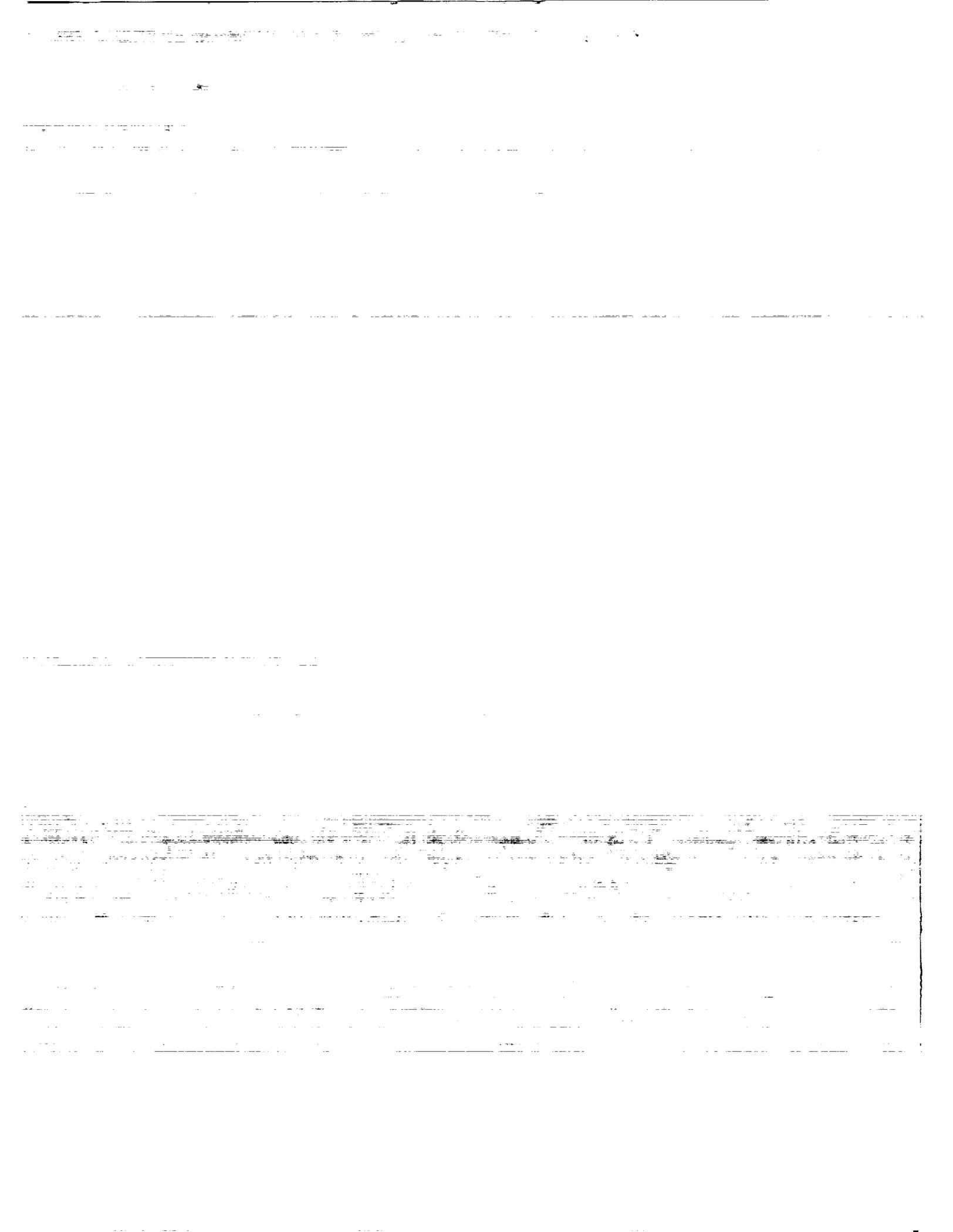
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Aloysius F. Hepp  
*Lewis Research Center*  
*Cleveland, Ohio*

Stan A. Duraj, Maria T. Andras,  
and William E. Eckles  
*Cleveland State University*  
*Cleveland, Ohio*

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## SYNTHESIS AND STRUCTURES OF METAL CHALCOGENIDE PRECURSORS

ALOYSIUS F. HEPP\*, STAN A. DURAJ,\*\* MARIA T. ANDRAS,\*\* AND WILLIAM E. ECKLES\*\*  
\* NASA Lewis Research Center, Mail Stop 302-1, Cleveland, OH 44135  
\*\* Department of Chemistry, Cleveland State University, Cleveland, OH 44115

### INTRODUCTION

Applications for non-oxide metal chalcogenides are numerous. Many applications take advantage of the photoelectrical or electrical properties of these materials as solar cells (e.g. CdS and CuInSe<sub>2</sub>); infrared detectors (e.g. Hg<sub>1-x</sub>Cd<sub>x</sub>Te and PbS) and other devices such as lasers [1]. Chevrel phases are superconducting, for example PbMo<sub>6</sub>S<sub>8</sub> has a T<sub>c</sub> of 15K [2]. An example of a chemical application is the use of heterogeneous systems such as Co-promoted molybdenum sulfide (Ni or W are sometimes substituted for Co and Mo) on  $\gamma$ -alumina catalysts for metal and sulfur removal under H<sub>2</sub> from crude oil, this allows the efficient and environmentally sound use of "dirtier" feedstocks [3]. Chemical sensitization to form AgAu<sub>x</sub>S<sub>y</sub> clusters on silver halide grains is an integral step in producing photographic emulsions [4]. It is interesting to note that there are many enzymes and electron transfer proteins with iron- and iron-molybdenum-sulfide cluster (e.g. ferredoxins and nitrogenase) active sites [5].

Structural and spectroscopic studies of metal chalcogenide cluster complexes enhance understanding of the chemical and electronic properties of these species in the solid state. A further motivation for this chemistry is the possible invention of novel precursors for solid state materials [6], with potentially improved properties. While there is tremendous activity and interest in the chemistry of compounds containing metal-sulfur, selenium, and tellurium bonds [7-9], the chemistry of electron deficient transition and main group metals is relatively underdeveloped. Our interest in species relevant to hydrodesulfurization catalysis led us to explore the reactivity of early transition metal sandwich complexes with sulfur-rich molecules such as dithiocarboxylic acids [10] and is continuing towards preparation of mixed metal sulfide complexes.

We have recently initiated work on precursors to CuInSe<sub>2</sub> and related chalcopyrite semiconductors. The very high radiation tolerance and the high absorption coefficient of CuInSe<sub>2</sub> makes this material extremely attractive for lightweight space solar cells. The potential for low-cost, high power-to-weight ratio, radiation resistant space solar cells has led to renewed interest in chalcopyrite semiconductors. We describe synthesis and structures of In- and Cu-chalcogenide complexes, and routes to precursors, illustrating our approach with an example from earlier work [10].

### EXPERIMENTAL

All manipulations of moisture and air-sensitive materials were done under an inert atmosphere by standard Schlenk techniques on a double-manifold vacuum line or in a Vacuum Atmospheres Co. glovebox equipped with a HE-493 dri-train. Solvents were freshly distilled from benzophenone ketyl prior to use. The metal sandwich compounds and CH<sub>3</sub>CSSH were synthesized as described in [10]. Metal compounds and powders were obtained from Strem Chemicals, Newburyport, MA. Chalcogenide-containing compounds were obtained from Aldrich Chemical Co., Milwaukee, WI. Electron impact mass spectra were recorded on a Finnigan TSQ-45 mass spectrometer. Single-crystal x-ray analyses, were done on an Enraf-Nonius CAD-4 diffractometer.

## RESULTS AND DISCUSSION

$(\eta^6\text{-C}_6\text{H}_6)_2\text{V}$  reacts with excess  $\text{CH}_3\text{CSSH}$  in toluene at  $25^\circ\text{C}$  for 4 days to produce  $[(\text{CH}_3\text{CS}_2)_2\text{V}(\mu\text{-}\eta^2\text{-S}_2)_2\text{V}(\text{S}_2\text{CCH}_3)_2]$ , **1**, in yields up to 62 % (figure 1). Brown crystals were grown by layering a benzene solution of **1** with heptane. The molecule crystallizes in the monoclinic space group,  $\text{P}2_1/\text{c}$ ; with cell constants of  $a = 10.425(2) \text{ \AA}$ ,  $b = 11.123(2) \text{ \AA}$ ,  $c = 9.133(4) \text{ \AA}$ ,  $\beta = 97.12(2)^\circ$ ; cell volume,  $V = 1051(1) \text{ \AA}^3$ ; and two molecules in the unit cell. An ORTEP diagram of **1** is shown in figure 1.

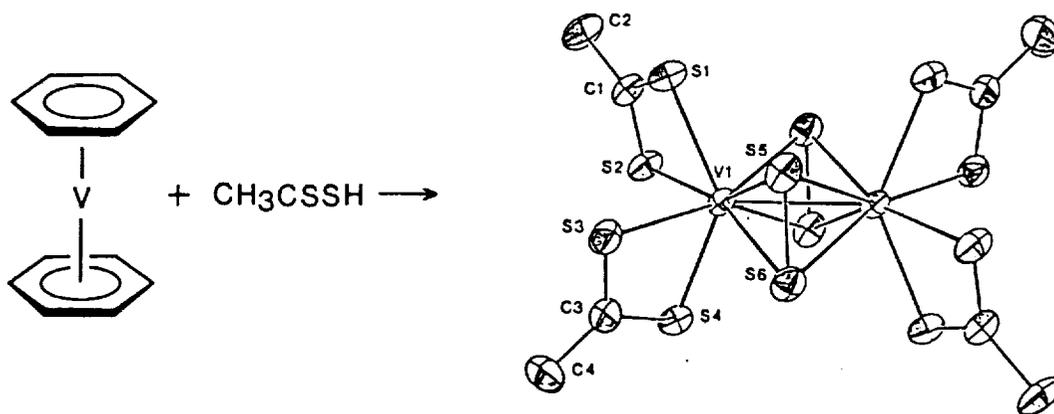


Figure 1. Chemical reaction leading to formation of **1**. ORTEP drawings of **1** also defines the labelling scheme. The thermal ellipsoids enclose 50% of electron density.

Magnetic susceptibility and structural data is consistent with a single bond between vanadium atoms with a V-V distance of  $2.800 \text{ \AA}$ ; the compound is diamagnetic as expected for a  $d^1\text{-}d^1$  unit. The V-V bond distance is nearly the same as the V-V bond distance in the tightly bound  $\text{V}(\mu\text{-}\eta^2\text{-S}_2)_2\text{V}'$  unit (V-V distance of  $2.83 \text{ \AA}$  [11]) in the mineral patronite,  $(\text{VS}_4)_n$  and is similar to a recently described V-V compound prepared from  $\text{VS}_4^{3-}$  and a dithiuram disulfide derivative (V-V distance of  $2.85 \text{ \AA}$  [12]). The stability of the  $\text{V}_2\text{S}_4$  core in **3** is evidenced by the identification of  $\text{V}_2\text{S}_4^+$  in the mass spectrum (70 eV, solid probe). The facile reaction between  $(\eta^6\text{-C}_6\text{H}_6)_2\text{V}$  and the sulfur-rich dithioacetic acid illustrates the potential utility of this approach to produce new metal-sulfide compounds. We have extended this chemistry to include several dithiocarboxylic acids and other low-valent metal compounds and metal powders including Cu, In, Zr, V, Hf, and Ta powders;  $\text{InCl}$ ,  $\text{Ga}_2\text{Cl}_4$ , and related halides; and other early transition metal sandwich compounds of Ti, Zr, V, and Nb [10,13].

Chemistry with other chalcogenide-rich molecules is under investigation to produce precursors for chalcopyrite semiconductors. In order to deposit thin films of metal chalcogenides on lightweight substrates such as polymers, low temperature chemical vapor deposition of volatile species must be employed. Further, to enhance control of stoichiometry it is desirable to use single-molecule precursors; this is one goal of our current research effort. Part of this effort entails the development of relevant aspects of In-, Ga-, and Cu-chalcogenide coordination and organometallic chemistry. Our approach is at all times to determine the structures of new intermediate or analogous compounds to enhance our understanding of the synthetic chemistry of precursor formation and to apply this understanding to the decomposition of candidate precursors.

Other chalcogenide-rich chemistry that is under investigation uses known oxidants like dialkyl- or diaryldichalcogenides and dithiuram derivatives, REER (E = S or Se, and R =  $-\text{CH}_3$ ,  $-\text{C}_6\text{H}_5$ , or  $-\text{CH}_2\text{C}_6\text{H}_5$ ; E = S; R =  $-\text{C}(\text{S})(\text{NR}_2)$ ). Reactions were generally carried out under inert atmosphere in coordinating

solvents. One example of a recently characterized compound is shown in figure 2.  $\text{Trans-Cl}_2\text{In}(\text{S-C}_6\text{H}_5)(\text{NC}_5\text{H}_4\text{CH}_3)_3$ , 2, is synthesized from simple starting materials producing clear rectangular prismatic crystals. The molecule crystallized in the monoclinic space group,  $P2_1/n$ ; with cell constants of  $a = 9.620(1) \text{ \AA}$ ,  $b = 17.601(5) \text{ \AA}$ ,  $c = 14.197(4) \text{ \AA}$ ,  $\beta = 99.28(2)^\circ$ ; cell volume,  $V = 2372(4) \text{ \AA}^3$ ; and four molecules to the unit cell.

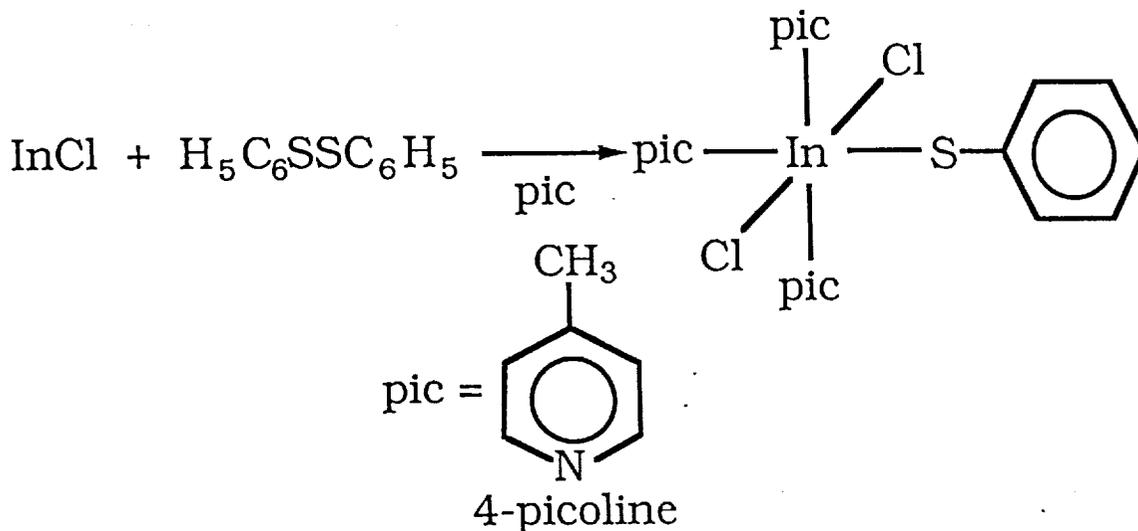


Figure 2. Chemical reaction leading to formation of 2. Diagram of 2 is shown on the right of the figure.

There are a number of synthetic studies of REER to prepare new compounds [14,15]. While similar compounds have been reported, this is the first structure of an indium compound with this coordination environment that has been determined. This molecule is easy to prepare and has five sites, two chlorides and three solvent ligands, for further chemistry. We have also prepared analogous compounds using different metals (Ga, Cu), ligands (-ER), and solvents. Reactions in tetrahydrofuran between metal powders and a dithiuram derivative produces black crystalline material after layering. X-ray diffraction studies failed to detect the presence of any metal sulfides. While it is known that dithiuram reacts with metal powders, no structures were reported [16]; we were only able to identify a known Ni complex [17]. We are currently investigating the structure of these molecules; the reaction chemistry to form precursors is currently underway.

## CONCLUSIONS

The use of low-valent  $\pi$ -bonded sandwich compounds and dithiocarboxylic acids as starting materials to prepare metal sulfur-containing complexes is novel and shows the potential for the development of facile syntheses of new metal sulfide compounds. We are currently extending this approach in two ways: using other chalcogenide-rich reactants with other low-valent metal complexes and metal powders. Precursors synthesized will be evaluated for the purity, morphology, and electrical properties of the materials produced.

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