intense in the CD and absorption spectra of an excited state has also been observed in the spectra of the excited triplet state of 4-thiouridine in tRNA.[64] The current work is the first comprehensive assignment of both the absorption and CD spectra of both the ground- and metastable excited-states of a molecular complex.

**Acknowledgment.** We thank V. M. Miskowski for helpful discussions and the National Institutes of Health for financial support under Grant GM35158.

---

(64) Milder, S. J.; Weiss, P. S.; Kliger, D. S. *Biochemistry* **1989**, *28*, 2258.

---

Contribution from the Department of Chemistry and Biochemistry and the Solid State Science Center,
University of California, Los Angeles, California 90024-1569

# Low-Temperature Precursor Synthesis of Crystalline Nickel Disulfide

Philippe R. Bonneau, Robert K. Shibao, and Richard B. Kaner*

*Received September 6, 1989*

Pure, crystalline nickel disulfide is synthesized within seconds from the solid-state reaction between potassium hexafluoronickelate(IV) and sodium pentasulfide hydrate at $\sim$65 °C. The nickel disulfide product is isolated by simply washing away the byproduct salts. The reaction is influenced by the hydration and the sulfur content of the sulfiding agent and by the transition-metal precursor. Increasing the hydration of the sodium pentasulfide or lowering the oxidation state of the nickel in potassium hexafluoronickelate from Ni(IV) to Ni(III) favors a less crystalline product. Reactions containing sulfiding agents with lower sulfur content, such as sodium monosulfide or sodium disulfide, produce mixtures of nickel monosulfide and nickel disulfide. X-ray diffraction, thermogravimetric analysis, and differential scanning calorimetry results are presented.

## Introduction

Crystalline transition-metal chalcogenides have traditionally been synthesized by reacting stoichiometric amounts of their constituent elements in evacuated silica tubes at 500–1200 °C.[1,2] Intermittent grinding and reheating are often necessary to obtain a pure phase. Precursor syntheses are important for providing lower temperature pathways and often more rapid methods of preparing known materials. Occasionally, new kinetically stable phases are discovered.[3] Some low-temperature precursor routes to group IV–VI transition-metal sulfides are known. These include metathesis reactions between transition-metal halides and alkali-metal sulfides carried out in nonaqueous solvents[4] or reactions between transition-metal halides and covalent sulfiding agents such as silyl sulfides.[5-7] Solution reactions generally produce finely divided materials that become crystalline only after annealing at elevated temperatures. Thermal decomposition of the precursors ammonium thiomolybdate and ammonium thiotungstate yields several molybdenum and tungsten sulfide phases.[8,9] In addition, thin films of some group VI and VIII transition-metal dichalcogenides can be prepared by reacting transition-metal carbonyls with a sulfur source.[10,11]

Low-temperature routes to group VIII transition-metal sulfides are not as well explored. Reactions between anhydrous hexachlorometalates(IV) and hydrogen sulfide at 110–250 °C produce poorly crystallized transition-metal dichalcogenides.[12,13] Anhydrous transition-metal chlorides react with ammonium hydrogen sulfide in polar organic solvents at room temperature.[14] The products of these reactions are amorphous materials. When anhydrous transition-metal sulfates are exposed to a mixture of hydrogen and hydrogen sulfide at 325–525 °C, metal-rich sulfides are formed.[15]

Delafosse and Barret prepared nickel disulfide from nickel sulfate and hydrogen sulfide at 230 °C.[16] Subsequent experiments by Bouchard, however, suggest that the products of this reaction are poorly crystallized, contain small amounts of water, and are extremely reactive toward oxidation in air.[17] Another route to nickel disulfide involves heating nickel monosulfide with excess sulfur. This reaction reportedly occurs at temperatures as low as 170 °C over a period of 40 h.[18] Our experience, however, has demonstrated that the starting materials must be very finely divided. If they are not, much higher temperatures ($\geq$450 °C) are required in order to obtain a pure, crystalline phase. Nickel metal and excess sulfur react at about 500 °C to produce nickel disulfide. Repeated grinding and firing with excess sulfur is needed to get a pure, single-phase material.[19]

We report here a quick, high-yield method for the preparation of crystalline nickel disulfide via a solid-state reaction that is initiated at low temperature. The synthetic method involves the reaction of a high-oxidation-state nickel fluoride complex with an alkali-metal sulfiding agent. The best precursors found are potassium hexafluoronickelate(IV) and sodium pentasulfide hydrate. This approach to the rapid low-temperature synthesis of nickel disulfide represents a model study for solid-state precursor syntheses that could be applicable to many other transition-metal chalcogenides.

## Experimental Section

Potassium hexafluoronickelate(IV), $K_2NiF_6$, was prepared by reacting a 2:1 mixture of potassium chloride and anhydrous nickel chloride (Alfa, ultrapure) with excess fluorine gas (98%, Spectra Gases) at 275 °C for approximately 6 h.[20] High-grade stainless-steel tubes were passivated with fluorine prior to loading the salts. All transfers of reagents and precursors were carried out in a He-filled drybox (Vacuum Atmo-

---

(1) Leith, R. M. A.; Terhell, J. C. J. M. Transition Metal Dichalcogenides. In *Preparation and Crystal Growth of Materials with Layered Structures*, Leith, R. M. A., Ed.; D. Reidel Co: Dordrecht, The Netherlands, 1977; pp 141–223.

(2) Brauer, G. *Handbook of Preparative Inorganic Chemistry*, 2nd ed.; Academic Press, Inc.: New York, 1965; Vols. 1 and 2.

(3) Murphy, D. W.; Cros, C.; DiSalvo, F. J.; Waszczak, J. V. *Inorg. Chem.* **1977**, *16*, 3027.

(4) Chianelli, R. R.; Dines, M. B. *Inorg. Chem.* **1978**, *17*, 2758.

(5) Martin, M. J.; Qiang, G.; Schleich, D. M. *Inorg. Chem.* **1988**, *27*, 2804.

(6) Bensalem, A.; Schleich, D. M. *Mater. Res. Bull.* **1988**, *23*, 857.

(7) Schleich, D. M.; Martin, M. J. *J. Solid State Chem.* **1986**, *64*, 359.

(8) Mering, J.; Levialdi, A. *C. R. Acad. Sci.* **1941**, *213*, 798.

(9) Sokol, L. *Coll. Czech. Chem. Commun.* **1956**, *21*, 1140.

(10) Chatzitheodorou, G.; Fiechter, S.; Kunst, M.; Luck, J.; Tributsch, H. *Mater. Res. Bull.* **1988**, *23*, 1261.

(11) Hofmann, W. K. *J. Mater. Sci.* **1988**, *23*, 3981.

(12) Passaretti, J. D.; Kaner, R. B.; Kershaw, R.; Wold, A. *Inorg. Chem.* **1981**, *20*, 501.

(13) Passaretti, J. D.; Dwight, K.; Wold, A.; Croft, W. J.; Chianelli, R. R. *Inorg. Chem.* **1981**, *20*, 2631.

(14) Passaretti, J. D.; Collins, R. C.; Wold, A. *Mater. Res. Bull.* **1979**, *14*, 1167.

(15) Pasquariello, D. M.; Kershaw, R.; Passaretti, J. D.; Dwight, K.; Wold, A. *Inorg. Chem.* **1984**, *23*, 872.

(16) Delafosse, D.; Barret, P. *C. R. Acad. Sci.* **1960**, *251*, 2964.

(17) Bouchard, R. J. *Mater. Res. Bull.* **1968**, *3*, 563.

(18) DeJong, W. F.; Willems, H. W. V. *Z. Anorg. Allg. Chem.* **1927**, *160*, 185. Biltz, W. *Ibid.* **1936**, *228*, 278.

(19) Bouchard, R. J. *J. Cryst. Growth* **1968**, *2*, 40.

(20) Klemm, W.; Huss, E. *Z. Anorg. Allg. Chem.* **1949**, *258*, 221. Klemm, W. *Angew. Chem.* **1951**, *63*, 396.

0020-1669/90/1329-2511$02.50/0 © 1990 American Chemical Society

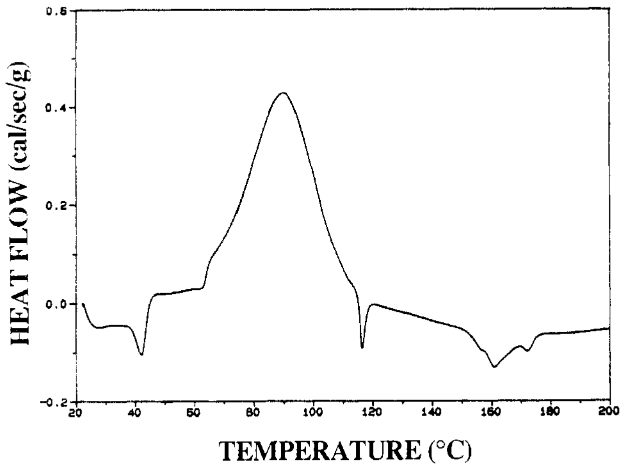

**Figure 1.** Differential scanning calorimetry of the reaction between potassium hexafluoronickelate(IV) and sodium pentasulfide hydrate.

spheres). Fluorination reactions were carried out on a metal vacuum line equipped with monel and stainless-steel fittings. Dark red potassium hexafluoronickelate(IV) was obtained in quantitative yield. Violet potassium hexafluoronickelate(III), $K_3NiF_6$, was prepared by reacting a 3:1 mixture of KCl and $NiCl_2$ as described by Stein et al.[21] Sodium monosulfide, $Na_2S$, and sodium disulfide, $Na_2S_2$, were obtained by reacting stoichiometric amounts of pure sodium and sulfur in liquid ammonia.[22] The ammonia was allowed to evaporate and the light yellow product was heated in vacuo to remove residual solvent. Sodium pentasulfide, $Na_2S_5$, was synthesized by combining $Na_2S_2$ with 3 equiv of elemental sulfur and heating the mixture to 500 °C in a sealed glass ampule.[23] $Na_5S_5 \cdot 0.06H_2O$, as well as slightly hydrated $Na_2S$ and $Na_2S_2$, were formed by stirring 1 g of anhydrous material in air for approximately 1 min. The weight increase was used to determine the amount of water present. $Na_2S_5$ exposed to 3 equiv of water yielded $Na_2S_5 \cdot 3H_2O$.

X-ray diffraction patterns were obtained with Ni-filtered Cu K$\alpha$ radiation at increments of 0.05° in $2\theta$ at 5 s/increment. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were carried out on Du Pont Analyzers Nos. 951 and 910, respectively. TGA of $NiS_2$ products were carried out in a stream of 5% $H_2$/95% $N_2$ gas. The temperature was increased 20 °C/min to 800 °C at which temperature the material remained until no further weight loss occurred (~4 h). DSC experiments were performed at 10 °C/min under argon.

## Results

When potassium hexafluoronickelate(IV) and 2 equiv of anhydrous sodium pentasulfide are combined and then sealed in a Pyrex tube under vacuum and heated, only a surface reaction is observed. The bulk of the reagents remain unreacted even at temperatures as high as 200 °C. However, if $K_2NiF_6$ is mixed with $Na_2S_5 \cdot 0.06H_2O$ (without grinding), sealed in an evacuated tube and heated to ~65 °C, a vigorous, exothermic reaction occurs in seconds. The reaction is given by eq 1. The product is isolated

$$K_2NiF_6 + 2Na_2S_5 \xrightarrow{0.12H_2O} NiS_2 + 4NaF + 2KF + 8S \qquad (1)$$

by washing with water, alcohol, and ether. Residual sulfur is removed by further washing with carbon disulfide. After the byproducts are removed, pure crystalline nickel disulfide remains.

The exothermic nature of the above reaction is illustrated in the DSC trace in Figure 1. The exotherm beginning at approximately 65 °C corresponds to the heat released during the bulk reaction. Because of the presence of a small endotherm at 117 °C, most probably due to the melting of the sulfur byproduct, the heat of reaction was determined by separate integration of the large exotherm and the tail located to the right of the small endotherm. Two baselines were created for the major peak. The first runs from the onset of the exotherm to a point on the left side of the endotherm, consistent with the baseline of the DSC trace. The second stretches from the onset of the exotherm to the onset of the endotherm. Integration of the area under the curve and above each baseline yields a range of 46–53 kcal/mol. The tail area to the right of the small endotherm represents approximately 4 kcal/mol.

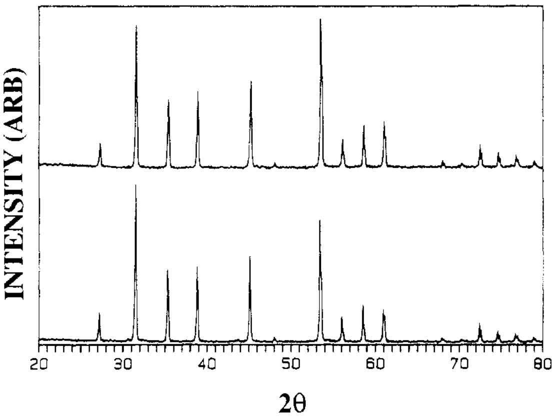

**Figure 2.** X-ray diffraction pattern of nickel disulfide made from nickel monosulfide and sulfur at 500 °C (top) and nickel disulfide prepared from the reaction of potassium hexafluoronickelate(IV) and sodium pentasulfide hydrate at ~65 °C (bottom).

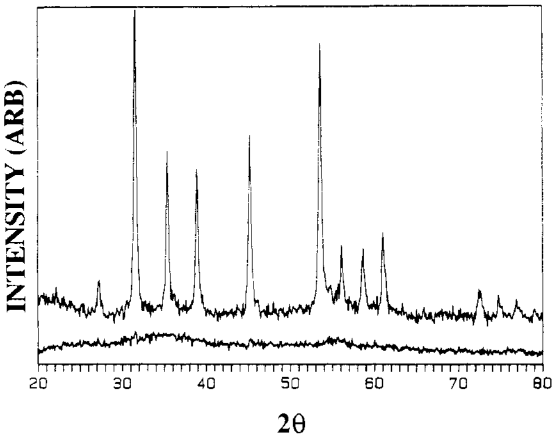

**Figure 3.** X-ray diffraction pattern of microcrystalline nickel disulfide formed in the reaction between $K_2NiF_6$ and $Na_2S_5 \cdot 3H_2O$ at ~65 °C (top) and the amorphous product formed in the reaction between $K_2NiF_6$ and $Na_2S_5$ in excess water at room temperature (bottom).

The crystallinity of the $NiS_2$ product is illustrated by its X-ray diffraction pattern (Figure 2, bottom). The X-ray diffraction pattern of $NiS_2$ obtained from NiS and sulfur ground together and heated at 500 °C for 4 days is presented for comparison (Figure 2, top). A TGA of 9.45 mg of the $NiS_2$ product obtained from the reaction of $K_2NiF_6$ and $Na_2S_5 \cdot 0.06H_2O$ left 4.52 mg of residue. This indicates a loss of exactly 2 equiv of sulfur and corresponds to the formula $NiS_{2.00}$. An X-ray diffraction pattern of the TGA residue revealed pure Ni.

When a more hydrated form of sodium pentasulfide, $Na_2S_5 \cdot 3H_2O$, is mixed with $K_2NiF_6$, an exothermic reaction again occurs at ~65 °C. The $NiS_2$ product that forms is much less crystalline (Figure 3, top). An approximate particle size determination was made by using the Scherrer equation[24] and the line broadening in this sample compared to that of a highly crystalline $NiS_2$ standard. On the basis of this calculation, the particle size of the $NiS_2$ product is ~260 Å. TGA on two different samples yielded 46.7% and 48.6% Ni residue. The theoretical value for $NiS_2$ is 47.8% Ni. Some of the microcrystalline $NiS_2$ product was then annealed in a sealed evacuated Pyrex tube for 1 day at 450 °C without excess sulfur. X-ray diffraction patterns taken after heat treatment revealed only phase-pure crystalline $NiS_2$.

When $K_2NiF_6$ is added to a solution of $Na_2S_5$ dissolved in a vast excess of water (~1 g reagents/25 mL of water), a reaction

---

(21) Stein, L.; Neil, J. M.; Alms, G. R. *Inorg. Chem.* **1969**, *8*, 2472.

(22) Klemm, W.; Sodomann, H.; Langmesser, P. *Z. Anorg. Allg. Chem.* **1939**, *241*, 281.

(23) Feher, F.; Berthold, H. J. *Z. Anorg. Allg. Chem.* **1953**, *273*, 144.

(24) Cullity, B. D. *Elements of X-ray Diffraction*; Addision-Wesley: Reading, MA, 1956.

occurs at room temperature. The purified nickel sulfide product is completely amorphous (Figure 3, bottom).

In separate experiments, $K_2NiF_6$ is combined with anhydrous $Na_2S$ and then anhydrous $Na_2S_2$. Once again the bulk of the reagents do not react under strictly anhydrous conditions even at temperatures as high as 200 °C. With slightly hydrated $Na_2S$ and $Na_2S_2$, both reactions occur at ~65 °C to produce NiS, $NiS_2$, KF, NaF, and excess S. The only significant difference between the two reactions is in the relative amounts of NiS and $NiS_2$ in the product mixture. The reaction of $K_2NiF_6$ with slightly hydrated $Na_2S_2$ produces significantly more $NiS_2$ than the reaction with slightly hydrated $Na_2S$.

If the Ni(III) salt, $K_3NiF_6$, is combined with $Na_2S_5{\cdot}0.06H_2O$, the reaction proceeds at low temperatures, but it does not appear to be as vigorous as the reaction with $K_2NiF_6$. The unsintered product is amorphous to X-rays, while the product after annealing at 450 °C is highly crystalline $NiS_2$.

## Discussion

Nickel disulfide forms in a pyrite structure.[25] The cubic lattice parameter *a* for $NiS_2$ determined from single crystal data is reported to be 5.6874 Å.[19] A least squares refinement of the X-ray data for $NiS_2$ produced by the precursor synthesis (Figure 2, bottom) yields a value of $a = 5.688$ (1) Å.

Nickel disulfide is normally synthesized from its constituent elements. Because solid–solid diffusion processes are slow, the reactants must be heated to temperatures of 450 °C or greater so that sulfur (bp = 434 °C) is in a gaseous state. Intermittent grinding, which increases the reactive surface area of the nickel or nickel monosulfide intermediate, and several days of heating with excess sulfur are required to get a pure nickel disulfide product.

The solid-state precursor synthesis has the advantage of reacting $Ni^{4+}$ (highest known oxidation state) in an enriched sulfur environment. Since the total of the enthalpies of formation of the products exceeds that of the reactants, product formation is quite favorable. The reaction is exothermic, and once initiated, it proceeds rapidly to produce a high yield of nickel disulfide. Traditionally, one of the difficulties of precursor syntheses is separating the product from the byproduct(s). In this case, however, the procedure is straightforward because the alkali-metal halide byproduct salts are very soluble in water and any excess sulfur can be extracted with carbon disulfide or carbon tetrachloride.

The above experiments demonstrate that reactions between potassium hexafluoronickelate and sodium sulfide are greatly affected by (1) the extent of hydration of the sulfiding agent, (2) the sulfur content of the sodium sulfide, and (3) the transition-metal precursor. Each of these three issues is treated in turn.

First, the reaction between potassium hexafluoronickelate(IV) and sodium pentasulfide is a solvent-assisted reaction. When pure anhydrous $Na_2S_y$ ($y$ = 1, 2, or 5) is combined with $K_2NiF_6$ and heated, the bulk of the reagents do not react even at temperatures as high as 200 °C. Only a surface reaction results. Without water present, the reaction does not proceed to any significant degree. Since a small amount of solvent is necessary to initiate the solid-state reaction at low temperatures, the difficulty then becomes the effective introduction of the solvent into the reaction. Direct addition of water decomposes the transition-metal precursor.[21] If, however, the water is mixed with $Na_2S_5$, it can be bound in the solid. The reagents can then be combined without reacting until they are heated.

The reaction between potassium hexafluoronickelate(IV) and slightly hydrated sodium pentasulfide begins at ~65 °C and goes rapidly to completion. Increasing the hydration of the sodium pentasulfide by using $Na_2S_5{\cdot}3H_2O$ still allows the reaction to proceed at ~65 °C. Complete solvation, i.e. with the reaction carried out in water, allows the reaction to proceed at room temperature. In all cases involving hydrated sulfiding agents, once the reactions begin, they proceed to completion in seconds. On the basis of results of experiments studying the effect of water on potassium hexafluoronickelates[21] and on the basis of present results, a plausible mechanism for initiation of these reactions involves aqueous attack on the precursor lattice, after which the reaction is driven by product formation.

Another important effect of solvent is to control the crystallinity of the nickel disulfide product. When $K_2NiF_6$ reacts with $Na_2S_5{\cdot}0.06H_2O$, the resulting product is highly crystalline $NiS_2$ with a particle size greater than 2000 Å (Figure 2, bottom). If the more hydrated $Na_2S_5{\cdot}3H_2O$ is used in the reaction, the $NiS_2$ is much less crystalline, with a particle size of ~260 Å (Figure 3, top). A vast excess of solvent in this reaction leads to completely amorphous $NiS_2$ (Figure 3, bottom). The more solvent added, therefore, the less crystalline the nickel disulfide product will be. This is likely a result of the solvent absorbing some of the heat evolved in this exothermic reaction. As the amount of solvent increases, the products experience much less local heating.

A DSC experiment carried out on amorphous $NiS_2$ reveals that crystallization begins at ~161 °C in a slightly exothermic process. If amorphous $NiS_2$ is the kinetic product, it is reasonable to assume that crystalline $NiS_2$ will only be produced when enough heat is available locally to initiate the crystallization process. The exothermic reaction between $K_2NiF_6$ and $Na_2S_5{\cdot}0.06H_2O$ must increase the temperature in the local environment of the product beyond the crystallization point. Any excess solvent acts as a heat sink, reducing local heating and therefore inhibiting crystallization.

Second, the reaction between potassium hexafluoronickelate(IV) and slightly hydrated sodium sulfide is greatly influenced by the sulfur content of the sodium sulfide. Reactions containing sodium pentasulfide lead exclusively to a nickel disulfide product. However, when slightly hydrated sodium disulfide or sodium monosulfide reacts with $K_2NiF_6$, both $NiS_2$ and NiS are formed. Any nickel monosulfide is undesirable because it is extremely difficult to separate from nickel disulfide. Sulfur-rich sulfiding agents are therefore used to favor the formation of $NiS_2$ over NiS. Since $NiS_2$ only forms in the presence of a sulfur-rich environment, such an environment must be locally available to each nickel cation. Hence, increasing $y$ to 5 in slightly hydrated $Na_2S_y$ yields pure $NiS_2$; conversely, lowering the sulfur content from $y = 5$ to 2 to 1 leads to proportionately more of the lower sulfide, NiS.

Third, the reactions are influenced by the transition-metal precursor. Reactions containing $K_2NiF_6$ are more vigorous and generate more heat than reactions containing $K_3NiF_6$, yet the molar quantities and species involved in both are similar, as can be seen by comparing eqs 1 and 2. The alkali-metal halide salts

$$K_3NiF_6 + {}^3\!/_2Na_2S_5 \xrightarrow{0.09H_2O} NiS_2 + 3NaF + 3KF + {}^{11}\!/_2S \quad (2)$$

formed in reactions 1 and 2 have total $\Delta H_f$ values of 821.9 and 820.3 kcal/mol, respectively.[26] The difference in thermodynamic driving force provided by the products is therefore negligible. The energies of formation of the transition-metal precursors, on the other hand, differ greatly. The reported values of $\Delta H_f$ for $K_2NiF_6$ and $K_3NiF_6$ are 469.2 and 611.3 kcal/mol, respectively.[27,28] It is therefore understandable that reaction 1 is more exothermic than reaction 2. Additionally, one could also argue that the reduction of Ni(IV) by $S_5^{2-}$ is a more energetic process than the reduction of Ni(III) by $S_5^{2-}$.

Slightly hydrated sodium pentasulfide reacts with $K_2NiF_6$ to form crystalline $NiS_2$ and with $K_3NiF_6$ to produce amorphous $NiS_2$. Since the former reaction is more exothermic than the latter, we believe that it generates more local heating. This in turn leads to a more crystalline nickel disulfide product.

In summary, the low-temperature-initiated reaction between potassium hexafluoronickelate and sodium pentasulfide requires

---

(25) Wells, A. F. *Structural Inorganic Chemistry*, 5th ed.; Claredon Press: Oxford, England, 1986.

(26) *JANAF Thermochemical Tables*, 3rd ed.; Lide, D. R., Jr., Ed.; American Chemical Society and American Institute of Physics, Inc.: New York, 1985.

(27) Hopkins, K. G. G.; Nelson, P. G. *J. Chem. Soc., Dalton Trans.* **1984**, *7*, 1393.

(28) Nelson, P. G.; Pearse, R. V. *J. Chem. Soc., Dalton Trans.* **1983**, *9*, 1977.

solvent activation, a sulfiding agent with a high sulfur content, and a high-oxidation-state metalate precursor if it is to produce highly crystalline $NiS_2$. Extension of this type of precursor synthesis to other transition-metal chalcogenides should be possible. Sodium sulfides were chosen as the sulfiding agents because of their wide range of stoichiometries ($Na_2S_y$, $y = 1, 2, 4$, and 5) and the high solubility of the sodium salt byproducts in water, but other alkali-metal sulfides could be used in place of sodium sulfide. In addition, alkali-metal selenides and alkali-metal tellurides can be prepared and should act as precursors to form transition-metal selenides and transition-metal tellurides. Other possible metal-containing precursors include binary halides in which the transition metal or main-group metal is stabilized in a high oxidation state. We are currently exploring precursor reactions involving the latter reagents.

## Conclusions

A rapid low-temperature solid-state synthesis of crystalline nickel disulfide has been developed. The best precursors found are $K_2NiF_6$ and $Na_2S_5\cdot0.06H_2O$. They react at ~65 °C in seconds to produce pure, crystalline nickel disulfide. The KF, NaF, and S byproducts can be easily removed by washing. The crystallinity of the nickel disulfide from the precursor reaction is comparable to the crystallinity of nickel disulfide prepared at 450-500 °C over several days from nickel monosulfide and sulfur or from the elements. Increasing the amount of water used in the precursor reaction or lowering the oxidation state of the transition metal results in lower crystallinity for the $NiS_2$ product. Lowering the sulfur content of the sodium sulfide reagent from $Na_2S_5$ to $Na_2S_2$ or $Na_2S$ leads to mixtures of nickel monosulfide and nickel disulfide.

**Acknowledgment.** This work was supported by the National Science Foundation, Grant No. CHE 8657822, through the Presidential Young Investigator Award Program along with matching funds provided by the ARCO Foundation.

---

Contribution from the Chemistry Departments, California State University, Sacramento, California 95819, and University of Hull, Hull HU6 7RX, U.K.

# The First Second-Row Triketone Complex Structure: Synthesis and Properties of a Substituted (1,3,5-Pentanetrionato)($\mu$-oxo)bis(dioxomolybdenum(VI))

Londa L. Borer*[,1a] and Ekkehard Sinn*[,1b]

*Received June 23, 1989*

Reaction of the $\beta$-triketone ligand 1,5-diphenyl-1,3,5-pentanetrione with molybdenum(VI) produces the first such derivatives with a second-row transition-metal element. The products are oxygen-bridged binuclear complexes, with structural resemblance to olefin epoxidation catalysts. When synthesized from ethanol solution, the product contains one molecule of ethanol per molecule of binuclear complex and is highly insoluble, suggesting a polymeric structure. When recrystallized from dimethyl sulfoxide, the product is a crystalline (1,3,5-pentanetrionato)($\mu$-oxo)bis((dimethyl sulfoxide)dioxomolybdenum(VI)) complex, shown by X-ray crystallography to have a coordinated DMSO on each molybdenum to make up a six-coordinated environment: Crystal data for $(MoO_2)_2(C_{17}H_{12}O_3)(O)(DMSO)_2$: space group $P2_1/n$ with $Z = 4$, $a = 8.093$ (3) Å, $b = 22.724$ (6) Å, $c = 14.087$ (6) Å, $\beta = 90.21$ (3)°; the structure was refined to an $R(F_o^2)$ value of 4.9% for 2240 reflections.

## Introduction

Interest in the $\beta$-polyketonate ligand systems stems from their ability to chelate two or more metal ions with the resultant formation of four-membered rings containing two metal atoms and two bridging oxygens. The complexes of the simpler 1,3-diketones have been well characterized, and recently chelates of 1,3,5-triketonates have received considerable attention. Several key papers have dealt with the structure, magnetism, and electrochemistry of Cu(II),[2] Ni(II),[3] Co(II),[4,5] Fe(III),[6] Cr(III),[7] and $V^{II}O$,[8] all first-row transition metals. Higher homologue chelates containing $UO_2$ have also been reported,[9] as have complexes of the hexadentate ligand generated by condensation of two triketones with diamines.[10] Mo(VI) complexes are of interest because these are known to catalyze such reactions as the epoxidation of olefins and the oxidations of alcohols.[11-13]

**Table I.** Crystal Data for a (1,3,5-Pentanetrionato)($\mu$-oxo)bis(dimethyl sulfoxide)dioxomolybdenum(VI) Complex, $(MoO_2)_2(C_{17}H_{12}O_3)(O)(DMSO)_2$

| | |
|---|---|
| $Mo_2S_2O_{10}C_{21}H_{24}$ | space group: $P2_1/n$ (No. 14) |
| fw = 692 | $T = 23$ °C |
| $a = 8.093$ (3) Å | $\lambda(\text{Mo K}\alpha) = 0.71069$ Å |
| $b = 22.724$ (6) Å | $\rho_{calc} = 1.78$ g/cm$^3$; $\rho_{obs} = 1.74$ g/cm$^3$ |
| $c = 14.087$ (6) Å | $\mu(\text{Mo K}\alpha) = 11.6$ cm$^{-1}$ |
| $\beta = 90.21$ (3)° | transm coeff = 0.91, 0.86 |
| $V = 2591$ (3) Å$^3$ | $R(F_o^2) = 0.049$ |
| $Z = 4$ | $R_w(F_o^2) = 0.062$ |

---

(1) (a) California State University. (b) University of Hull.

(2) (a) Fenton, D. E.; Schroeder, R. R.; Lintvedt, R. L. *J. Am. Chem. Soc.* **1978**, *100*, 6. (b) Lintvedt, R. L.; Kramer, L. S. *Inorg. Chem.* **1983**, *22*, 796. (c) Lintvedt, R. L.; Ranger, G.; Schoenfelner, B. A. *Inorg. Chem.* **1984**, *23*, 688.

(3) Lintvedt, R. L.; Ranger, G.; Ceccarelli, C. *Inorg. Chem.* **1985**, *24*, 2359.

(4) Glick, M. D.; Lintvedt, R. L. *Prog. Inorg. Chem.* **1978**, *21*, 233 and references cited therein.

(5) Lintvedt, R. L.; Tomlonovic, B. K.; Fenton, D. E.; Glick, M. D. *Adv. Chem. Ser.* **1976**, *No. 50*, 407.

(6) Borer, L. L.; Vanderbout, W. *Inorg. Chem.* **1979**, *18*, 526.

(7) Borer, L. L.; Horsma, R.; Rajan, O. A.; Sinn, E. *Inorg. Chem.* **1986**, *25*, 3652.

(8) Lintvedt, R. L.; Glick, M. D.; Tomlonovic, B. K.; Gavel, D. P. *Inorg. Chem.* **1976**, *15*, 1646.

(9) Lintvedt, R. L.; Schoenfelner, B. A.; Ceccarelli, C.; Glick, M. D. *Inorg. Chem.* **1984**, *23*, 2867.

(10) (a) Ahmad, N. *Inorg. Chim. Acta* **1989**, *155*, 237. (b) Casellato, U.; Vigato, P. A.; Fenton, D. E.; Vidali, M. *Chem. Soc. Rev.* **1979**, *8*, 199. (c) Fenton, D. E.; Gayda, S. E. *J. Chem. Soc., Dalton Trans.* **1977**, 2095, 2102, 2109. (d) Vigato, P. A.; Casellato, U.; Tamburini, S.; Milani, F.; Musiani, M. M. *Inorg. Chim. Acta* **1982**, *61*, 89.

(11) Bortolini, O.; Conte, V.; DiFuria, F. D.; Modena, G. *Nouv. J. Chim.* **1985**, *9*, 147.

(12) Sheldon, R. H.; van Doorn, J. A. *J. Catal.* **1973**, *31*, 427.

(13) Bortolini, O.; DiFuria, F.: Modena, G. *J. Mol. Catal.* **1982**, *14*, 53.

0020-1669/90/1329-2514$02.50/0 © 1990 American Chemical Society