6084 Inorg. Chem. 1993, 32, 6084–6087

High-Quality Mixed-Transition-Metal Dichalcogenides from Solid-State Exchange Reactions

Philippe R. Bonneau and Richard B. Kaner*

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

Received June 3, 1993[⊗]

High-quality molybdenum–tungsten disulfide solid solutions, $(Mo,W)S_2$, are rapidly synthesized in self-propagating, solid-state precursor reactions between $(MoCl_5{\cdot}WCl_6)$ and Na_2S. The mixed-metal dichalcogenide products can be readily reduced in a dilute hydrogen atmosphere at approximately 900 °C to the corresponding Mo–W alloys. The metal distribution in the Mo–W alloys is examined using the high-angle 123 powder X-ray reflection and can be correlated to the metal distribution in the metal dichalcogenide product. A comparative study of the peak profiles of several alloys and standards shows that this precursor approach yields mixed-metal dichalcogenide products with a better metal dispersion than the products of long-term, high-temperature reactions between the elements. Powder X-ray diffraction data, as well as elemental and thermogravimetric analyses, are presented.

Introduction

Early-transition-metal dichalcogenides have been the focus of many studies. Their layered structures are responsible for a widely diverse, intriguing intercalation chemistry[1-3] and applications as solid lubricants,[4,5] cathode materials,[6,7] hydrodesulfurization catalysts,[8-10] and photoelectrochemical (PEC) cells.[11-15] Additionally, the structural, electronic, and magnetic properties of these materials can be systematically manipulated by the substitution of the metal[16] or the chalcogen[17-19] to produce a large number of solid-solution compounds. Ternary, as well as binary, dichalcogenides are frequently prepared by reacting the elements in evacuated silica tubes at 700–1000 °C for several days to a few weeks.[20] Repeated grinding and heating are necessary in many cases to attain a single-phase product.

A different approach to the synthesis of mixed-metal dichalcogenides was introduced by Bouchard.[21] This technique involved heating solid-solution metal sulfates in the presence of H_2S/N_2 at 350 °C. The use of isomorphous solid-solution precursors provides several advantages over traditional high-temperature syntheses. First, precursors are more reactive starting materials than elements. Second, solid-solution precursors contain an intimate mixture of the product constituents. As a result, shorter reaction times and lower temperatures are required.

Mixed-metal precursor routes have mainly been applied to the preparation of ternary dichalcogenides of the later transition metals.[21,22] The present study, on the other hand, shows that mixed-metal dichalcogenides of the early transition metals can now be prepared in solid-state reactions between mixed-transition-metal halide precursors and alkali-metal chalcogenide reagents. The solid-solution precursor syntheses quickly and conveniently form high-quality ternary phases. Recently, we reported the successful implementation of analogous reactions for the preparation of binary materials.[23]

Molybdenum–tungsten dichalcogenide products can be reduced to the corresponding alloys by heating in the presence of hydrogen. The metal distribution in the alloy is examined by powder X-ray diffraction and related to the homogeneity in the parent compound. The preparation of alloys, especially refractory alloys, from the decomposition of isomorphic mixed-metal precursors was fairly recently explored. For example, the coprecipitation of ammonium paramolybdate and ammonium paratungstate from a water–alcohol mixture leads to the formation of the homogeneous heteropolymetalate $(NH_4)_6(Mo_{7-n}W_nO_{24}){\cdot}4H_2O$. Reduction of this intermediate[24,25] or $(Mo,W)O_3$[26,27] under hydrogen at 600–800 °C yields Mo–W alloys. This approach has also been extended to W–Re alloys[28,29] and alloys of the platinum group metals.[30] Since molybdenum and tungsten are refractory metals, mp 2610 and 3410 °C, respectively, their alloys are typically prepared from high-temperature melts or by sintering the metals in a powder form for 10–12 h at ~2300 °C.[31]

[⊗] Abstract published in *Advance ACS Abstracts,* November 15, 1993.

(1) Whittingham, M. S.; Jacobson, A. J., Eds. *Intercalation Chemistry*; Academic Press: New York, 1982.

(2) Divigalpitiya, W. M. R.; Frindt, R. F.; Morrison, S. R. *Science* **1989**, *246*, 369.

(3) Miremadi, B. K.; Morrison, S. R. *J. Appl. Phys.* **1990**, *67*, 1515.

(4) Clauss, F. L. *Solid Lubricants and Self-Lubricating Solids*; Academic Press: New York, 1972.

(5) Lince, J. R.; Fleischauer, P. D. *J. Mater. Res.* **1987**, *2*, 827.

(6) Rouxel, J.; Brec, R. *Annu. Rev. Mater. Sci.* **1986**, *16*, 137.

(7) Auborn, J. J.; Barberio, Y. L.; Hansen, K. J.; Schleich, D. M.; Martin, M. J. *J. Electrochem. Soc.* **1987**, *134*, 580.

(8) Chianelli, R. R. *Catal. Rev.—Sci. Eng.* **1984**, *26*, 361.

(9) Pecoraro, T. A.; Chianelli, R. R. *J. Catal.* **1981**, *67*, 430.

(10) Gobolos, S.; Wu, Q.; Delannay, F.; Grange, P.; Delmon, B. *Polyhedron* **1986**, *5*, 219.

(11) Tributsch, H. In *Modern Aspects of Electrochemistry*; Bockris, J. O. M., Conway, B. E., White, R. E., Eds.; Plenum: New York, 1986; Vol. 17.

(12) Lewerenz, H. J.; Tributsch, H.; Spiesser, M. *J. Electrochem. Soc.* **1985**, *132*, 700.

(13) Kline, G.; Kam, K.; Canfield, D.; Parkinson, B. A. *Sol. Energy Mater.* **1981**, *4*, 301.

(14) Lewerenz, H. J.; Heller, A.; DiSalvo, F. J. *J. Am. Chem. Soc.* **1980**, *102*, 1877.

(15) Tributsch, H. *J. Electrochem. Soc.* **1978**, *125*, 1068.

(16) Hodul, D. T.; Stacy, A. M. *J. Solid State Chem.* **1986**, *62*, 328.

(17) Schneemeyer, L. F.; Sienko, M. J. *Inorg. Chem.* **1980**, *19*, 789.

(18) Mentzen, B. F.; Sienko, M. J. *Inorg. Chem.* **1976**, *15*, 2198.

(19) Agarwal, M. K.; Patel, P. D.; Joshi, R. M. *J. Mater. Sci. Lett.* **1986**, *5*, 66.

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

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

(22) Passaretti, J. D.; Chianelli, R. R.; Wold, A.; Dwight, K.; Covino, J. *J. Solid State Chem.* **1986**, *64*, 365.

(23) Bonneau, P. R.; Jarvis, R. F., Jr.; Kaner, R. B. *Nature* **1991**, *349*, 510.

(24) Cheetham, A. K. *Nature* **1980**, *288*, 469.

(25) Cheetham, A. K.; Chowdhury, A. J. S. *J. Less-Common Met.* **1986**, *116*, 43.

(26) Skorokhod, V. V.; Solonin, Y. M. *Poroshk. Metall. (Minsk)* **1983**, *7*, 18.

(27) Skorokhod, V. V.; Solonin, Y. M.; Privalov, Y. G. *Poroshk. Metall. (Minsk)* **1984**, *3*, 1.

(28) Cheetham, A. K.; Chowdhury, A. J. S. *Proc. Plansee Seminar, 10th* **1981**, *3*, 135.

(29) Radchenko, O. G.; Uvarova, I. V. *Nov. Porosh. Kompozits. Neorgan. Mater. (Kiev)* **1983**, 3.

(30) Chowdhury, A. J. S.; Cheetham, A. K.; Cairns, J. A. *J. Catal.* **1985**, *95*, 353.

0020-1669/93/1332-6084$04.00/0

Table I. Analysis of MoW Ratios in (Mo,W)S_2 Solid Solutions

	stoichiom of product				
precursor	theor	expected[a]	powder X-ray diffr	elemental anal.	TGA
$MoCl_5 \cdot WCl_6$	$Mo_{0.50}W_{0.50}$	$Mo_{0.65}W_{0.35}$	$Mo_{0.68}W_{0.32}$	$Mo_{0.67}W_{0.33}$	$Mo_{0.67}W_{0.33}$
$MoCl_5 \cdot WCl_6$	$Mo_{0.50}W_{0.50}$	$Mo_{0.65}W_{0.35}$	$Mo_{0.73}W_{0.27}$		
$MoCl_5 \cdot WCl_6$	$Mo_{0.50}W_{0.50}$	$Mo_{0.65}W_{0.35}$	$Mo_{0.68}W_{0.32}$	$Mo_{0.66}W_{0.34}$	$Mo_{0.64}W_{0.36}$
$MoCl_5 \cdot WCl_6$	$Mo_{0.50}W_{0.50}$	$Mo_{0.65}W_{0.35}$	$Mo_{0.68}W_{0.32}$		
$MoCl_5 \cdot WCl_6$	$Mo_{0.50}W_{0.50}$	$Mo_{0.65}W_{0.35}$	$Mo_{0.70}W_{0.30}$		
$2MoCl_5 \cdot WCl_6$	$Mo_{0.67}W_{0.33}$	$Mo_{0.79}W_{0.21}$	$Mo_{0.83}W_{0.17}$		$Mo_{0.80}W_{0.20}$
$MoCl_5 \cdot 2WCl_6$	$Mo_{0.33}W_{0.67}$	$Mo_{0.48}W_{0.52}$	$Mo_{0.50}W_{0.50}$		$Mo_{0.48}W_{0.52}$

[a] Based on reaction yields.

Experimental Section

Molybdenum pentachloride (Johnson Matthey/Aesar, 99.6%) and tungsten hexachloride (Johnson Matthey/Aesar) are resublimed in an evacuated, sealed Pyrex tube (25 mm o.d. × 25 cm) in a temperature gradient where T_1 = 250 °C and T_2 = room temperature. The hexachloride rather than the pentachloride of tungsten was used because of its relative stability and greater availability. Resublimation is required in order to separate the desired molecular precursor from any lower-valent metal chlorides and metal oxychloride contaminants. The molecular precursor(s) and the metal oxychloride impurities are very volatile and rapidly transport to the cooler end of the temperature gradient. The metal oxychlorides condense farthest from the hot zone. The best separation is achieved if the transport tube is removed from the furnace after most of the dense vapor of the higher-valent metal chlorides has recondensed. The tube is allowed to cool to room temperature and is then opened under inert atomsphere.

Previous studies demonstrate that the success of these metathesis reactions is strongly dependent upon the careful, yet facile, preparation of the precursors. Because the molecular metal chlorides have significantly different vapor pressures, cosublimation is not recommended for the preparation of solid solutions. In fact, it leads to a considerable compositional gradient in the recondensed solid that can vary appreciably from one run to another depending on the transport conditions. Since the composition of the reagent crystals in turn determines the composition of the mixed-metal dichalcogenide product, large compositional gradients in the precursors must be avoided. More consistent results are obtained by melting the metal chloride mixture at 300 °C in an evacuated, sealed Pyrex tube only slightly larger than the volume of the melt. The limited volume ensures that only a very small amount of the precursor mixture is vaporized and that the stoichiometry in the liquid is essentially identical to that of the original solid mixture. The melt is removed from the furnace and then vigorously shaken until it solidifies. This approach appears to minimize, if not virtually eliminate, drastic compositional gradients in the precursors. Sodium sulfide is prepared by reacting stoichiometric amounts of the elements in liquid ammonia and by sintering the finely divided product at 600 °C for 12 h.[32]

The mixed-metal dichalcogenides are produced by ignition of a mixture of metal–chloride precursor (0.5–1.0 g) and a stoichiometric amount of alkali-metal chalcogenide with a hot filament in a stainless-steel bomb.[33] The products are then isolated by washing with methanol, water, and ether. Residual sulfur is removed by briefly heating the product with a heat gun while it is drying on a vacuum line.

Powder X-ray diffraction of the mixed-metal chloride precursors and mixed-metal dichalcogenide products was carried out in steps of 0.05° 2θ at a rate of 5 s/step on a GE diffractometer equipped with Ni-filtered Cu Kα radiation. The mixed-metal chloride precursors are very air- and moisture-sensitive and are therefore covered with a protective Mylar film during the X-ray procedure. The stoichiometries of the mixed-metal dichalcogenides were determined by elemental (Galbraith Laboratories, Inc., Knoxville, TN) and/or thermogravimetric analyses (DuPont 9900 thermal analysis system). In the latter analyses, the solid-solution dichalcogenides were decomposed in 5% H_2/95% N_2 until no further weight loss occurred (24–30 h). Powder X-ray diffraction of the TGA residues, or alloys, was carried out on a STOE transmission diffractometer with CuKα_1 radiation.

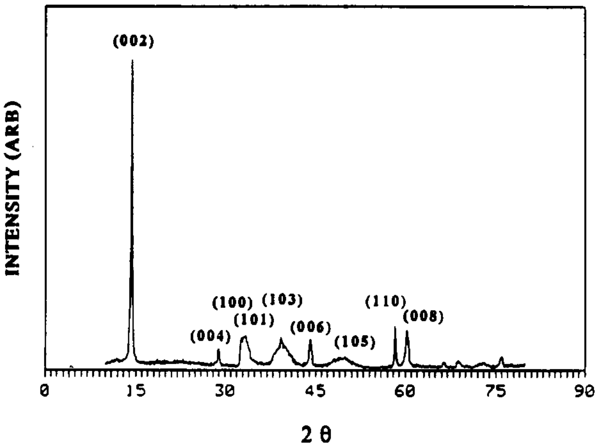

Figure 1. Powder X-ray diffraction pattern of (Mo,W)S_2 formed in the reaction of $MoCl_5 \cdot WCl_6$ and Na_2S.

Results and Discussion

Molybdenum pentachloride and tungsten hexachloride form a homogeneous melt whose color is a mixture of those of the pure binary components. A crystal structure for the molecular mixture was not determined because satisfactory single crystals could not be obtained from the resolidified melts. Powder X-ray diffraction, however, reveals three peaks at 15.70, 33.30, and 43.70°. The positions of these reflections do not correspond to the data for the individual, purified binary halides.

As expected, the intimate mixture of high-valent metal chlorides reacts vigorously with sodium sulfide to form excellent mixed-metal dichalcogenides in just seconds (eq 1).

$$(MoCl_5 \cdot WCl_6) + (n/2)Na_2S \rightarrow (Mo,W)S_2 + nNaCl + (n/2 - 2)S \quad (1)$$

$$n = \text{mol of } Cl^-$$

These self-sustaining reactions are very exothermic and produce heats in excess of 700 kJ/mol.[23] Table I summarizes the metal ratios in several (Mo,W)S_2 samples determined from elemental and thermogravimetric analyses. The powder X-ray diffraction pattern of a washed (Mo,W)S_2 sample is shown in Figure 1. Powder X-ray analysis of (Mo,W)S_2 solid solutions, however, cannot be used to unambiguously confirm the relative metal composition. The lattice parameters for MoS_2 (a = 3.1616 Å, c = 12.2938 Å)[17] and WS_2 (a = 3.161 Å, c = 12.358 Å)[18] are not appreciably different, and high-angle lines (>90° 2θ) are not intense enough to permit satisfactory determination of the solid-solution stoichiometry. Molybdenum and tungsten form a continuous body-centered-cubic solid solution in which the lattice parameter varies linearly with composition between 3.1472 Å (Mo) and 3.1648 Å (W).[34] Furthermore, molybdenum and tungsten possess sufficiently intense 222 and 123 diffraction peaks, and the separation between molybdenum and tungsten lines at

---

[31] Timofeeva, A. A.; Bulat, I. B.; Voronin, Y. V.; Fedoseev, G. K.; Karasev, V. M. *Porosh. Metall. (Minsk)* **1984**, *10*, 35.

[32] Klemm, W.; Sodomann, H.; Langmesser, P. *Z. Anorg. Allg. Chem.* **1939**, *241*, 281.

[33] Bonneau, P. R.; Wiley, J. B.; Kaner, R. B. *Inorg. Synth.*, in press.

[34] Nagender Naidu, S. V.; Sriramamurthy, A. M.; Rama Rao, P. *Bull. Alloy Phase Diagrams* **1984**, *5*, 177.

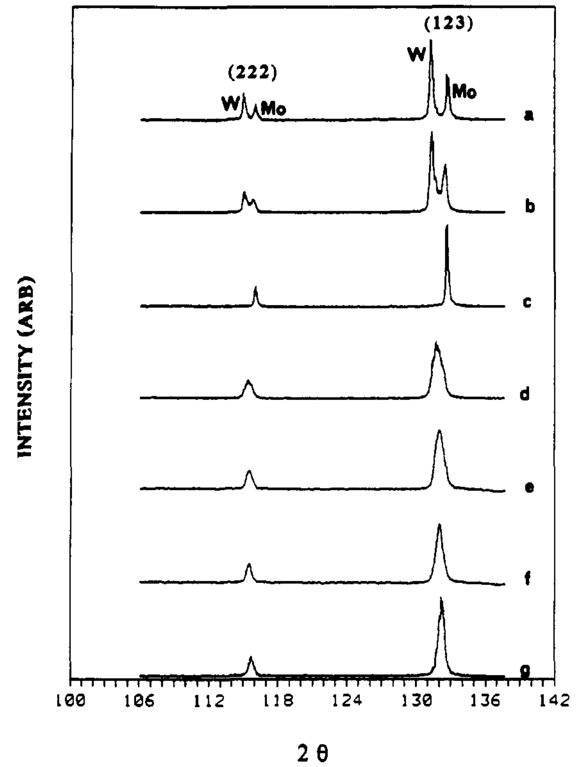

Figure 2. Powder X-ray diffraction patterns (a) Mo and W heated at 1000 °C for 6 days; (b–g) pure metals or alloys resulting from the reduction of the indicated compounds with H_2 at 920–950 °C for 24–30 h; (b) physical mixture of MoS_2 and WS_2; (c) MoS_2; (d) $Mo_{0.5}W_{0.5}S_2$ prepared from the elements at 1000 °C, 4 days; (e) $Mo_{0.5}W_{0.5}S_2$ from the elements at 1000 °C, 2 weeks; (f) $Mo_{0.5}W_{0.5}S_2$ from the elements at 1000 °C, 4 weeks; (g) $(Mo,W)S_2$ from a reaction between $MoCl_5{\cdot}WCl_6$ and Na_2S.

high angles provides an ideal method for the analysis of the metal ratio in $(Mo,W)S_2$ samples. Molybdenum–tungsten dichalcogenide products are therefore decomposed in hydrogen to yield Mo–W alloys. The alloys are then compared to standards of Mo and W metals and to a $Mo_{0.5}W_{0.5}$ alloy prepared from the reduction of a $Mo_{0.5}W_{0.5}S_2$ sample synthesized from the elements at high temperatures. Calculations of alloy stoichiometries are based on the positions of the 123 peaks of the alloys relative to the same lines for the standards. These results are also presented in Table I.

Powder X-ray analyses are important not only in the determination of alloy compositions but also in the evaluation of the relative qualities of various preparations. In Figure 2, Mo and W controls are compared to various Mo–W alloys produced by reducing $(Mo,W)S_2$ samples in dilute hydrogen at 920–950 °C for ~24 h. Mo and W (Figure 2a) heated to 1000 °C for 6 days show virtually no evidence of alloying, normally reflected in an increased intensity between the 222 or 123 diffraction peaks. This result agrees with a previous study of the interdiffusion of Mo and W, in which the first signs of solid-solution formation during the sintering of 85% W/15% Mo and 50% W/50% Mo were detected only after ~5 h at 1400 °C.[31] The second control (Figure 2b) is the product of the reduction of a physical mixture of MoS_2 and WS_2. The reduction of metal disulfides in a dilute hydrogen atmosphere produces H_2S, creating a very dynamic system which could potentially lead to alloying. The decomposition of the MoS_2/WS_2 mixture, however, forms only a small amount of alloy. The reduction of a physical mixture of MoO_3 and WO_3 in hydrogen yields similar results.[25] The final control (Figure 2c) is Mo from the decomposition of pure MoS_2. When compared to a sintered Mo standard, the Mo residue reveals virtually no broadening of the diffraction peaks. The decomposition/sintering process, therefore, does not lead to any appreciable particle size broadening. The X-ray diffraction patterns of the alloys resulting from the reduction of several $Mo_{0.5}W_{0.5}S_2$ samples prepared from the elements at 1000 °C for 4 days, 2 weeks, and 4 weeks, respectively, are shown in Figure 2d–f. The signs of slow solid–solid diffusion are evident, even considering the appreciable vapor pressure of metal sulfides relative to the vapor pressures of the pure metals. The constituent metal particles react quickly with sulfur to form metal disulfides, yet interdiffusion of the metal components is relatively slow, requiring prolonged heating at elevated temperatures. The longer the parent metal disulfide compound is heated, the less broadening is observed in the respective alloy, indicating an increase in homogeneity. Finally, decomposition of $(Mo,W)S_2$ from the rapid, solid-state precursor synthesis yields the diffraction pattern in Figure 2g. The width of the 123 line at half-height indicates that this alloy is considerably more homogeneous than the alloys from the 4-day and 2-week preparations, and even slightly better than the one from the 4-week preparation.

The diffraction patterns in Figure 2 illustrate the relationship between peak profile and alloy homogeneity. The narrower the alloy diffraction lines, the more uniform the metal mixture. Under identical reduction conditions, the alloys originating from the reduced products of precursor reactions exhibit an equal or superior degree of homogeneity than alloys resulting from the reduced products of traditional high-temperature reactions. The comparative study of molybdenum–tungsten alloys therefore clearly demonstrates that precursor routes to mixed-metal dichalcogenides are an attractive alternative to time- and energy-consuming syntheses from the elements at elevated temperatures.

Powder X-ray analysis of alloys is a good relative indicator of the metal distribution in mixed-metal compounds, provided the alloy samples and standards are prepared under identical conditions. The metal distribution in the alloy from the precursor synthesis does not, however, necessarily reflect the absolute metal distribution either in the mixed-metal halide precursor or in the mixed-metal dichalcogenide product. Since molybdenum pentachloride normally exists as a dimeric species and tungsten hexachloride as a monomeric species, product inhomogeneity may be the result of ordering that begins in the precursor mixture. Furthermore, the molecular species in the metal–halide mixture do not have the same reactivities. Metal clustering may therefore occur because the molybdenum pentachloride component is preferentially reduced by the alkali-metal chalcogenide. If these factors are indeed partially responsible for clustering, then substitution of WCl_6 with WCl_5, isostructural[35] and isoelectronic with $MoCl_5$, may be an improvement. Finally, ordering may take place in the final step as the metal dichalcogenide product decomposes. In certain systems, the decomposition temperature must be carefully chosen so that phase separation of the solid-solution compound does not precede formation of the alloy.[27] Inhomogeneity may therefore result from slightly different decomposition rates between MoS_2 and WS_2. This phenomenon, however, has not been studied in the $(Mo,W)S_2$ system.

An important, and often exploited, characteristic of many precursor reactions is that they usually tend to proceed stoichiometrically. Ideally, the components in a solid-solution precursor should react uniformly so that the desired product stoichiometry is determined solely by the precursor stoichiometry. A very interesting characteristic of the above precursor reactions, however, is that the metal ratio in the mixed-metal halide precursor is not conserved in the mixed-metal dichalcogenide product. This phenomenon can be explained by the differing reactivities of the constituent species, molybdenum pentachloride and tungsten hexachloride. Molybdenum pentachloride exists in a +5 oxidation state, somewhat unusual for group VI metals. It presumably stabilizes itself by dimerizing in both the solid and gaseous states, up to ~200 °C.[36,37] Above 300 °C, spectroscopic evidence and

---

[35] Remy, H. In *Treatise on Inorganic Chemistry*, Kleinberg, J., Ed.; Elsevier Publishing Co: New York, 1956; Vol. 2, p 175.

pressure measurements indicate that molybdenum pentachloride dissociates into trigonal bipyramidal monomers.[36] Furthermore, molybdenum pentachloride is a labile d^1 complex readily reduced by strong Lewis bases. Tungsten hexachloride is more coordinatively saturated than Mo(V), possesses a d^0 configuration, and is relatively stable. Although it contains a higher-oxidation-state metal, tungsten hexachloride is apparently not as easily reduced by sodium sulfide as molybdenum pentachloride. The results of reactions between the individual binary halides and sodium sulfide support this conclusion. Molybdenum disulfide is produced in 80% yield when molybdenum pentachloride reacts with sodium sulfide on a gram scale. A similar mass reaction leading to tungsten disulfide, on the other hand, produces only a 43% yield. Although the yields can be affected by the total amount of reagents used and the reaction conditions, the ratio of the yields under identical reaction conditions does appear to be significant. If the starting precursor is $MoCl_5 \cdot WCl_6$, then the expected mixed-metal dichalcogenide product, on the basis of an approximate yield ratio of 80/43 or 1.86, is $Mo_{0.65}W_{0.35}S_2$. The experimental stoichiometries of the first five samples listed in Table I closely agree with this calculated stoichiometry. Furthermore, elemental, thermogravimetric, and X-ray analyses of the molybdenum/tungsten ratios in the transition-metal dichalcogenide samples prepared from the other molybdenum–tungsten chloride precursors also closely coincide with the expected metal stoichiometries in the products. The relationship between the molar concentration of molybdenum in the precursor and the molar concentration of molybdenum in the product, assuming independent reaction of molybdenum pentachloride and tungsten hexachloride, is plotted in Figure 3. The solid curve is the best fit of several calculated data points (open triangles). The overlayed experimental data (solid triangles), determined by thermogravimetric analysis of the metal dichalcogenide product, conform quite well to the theoretical curve. These results indicate that the molecular components in the solid-solution reagents indeed appear to react independently.

Two straightforward approaches to compensate for the different reactivities of molybdenum pentachloride and tungsten hexachloride exist. The first is to adjust the relative concentrations of the components in the precursor according to Figure 3 so that the approximately desired stoichiometry in the product will be obtained. The other approach would be to substitute WCl_5 for WCl_6. The molybdenum and tungsten pentachlorides should have similar reactivities and even codimerize to form excellent solid-solution precursors.

Several other mixed-metal dichalcogenides are accessible with this method. The solid-solution precursor $(Mo,Nb)Cl_5$ reacts with Na_2Se to yield $(Mo,Nb)Se_2$. Furthermore, $MoCl_5$, WCl_5, $NbCl_5$, and $TaCl_5$, all low-melting molecular solids, can conceivably be mixed in any combination or in any ratio to form a large number of mixed-metal halide precursors which could then be simply reacted with the appropriate anion reagent. Additional studies would be needed, however, in order to determine the relative reactivities of each metal–halide species with alkali-metal chalcogenides. Precursor compositions could then be adjusted to yield products with the desired stoichiometries. Rapid solid-state metathesis reactions have also been successfully applied to the preparation of transition-metal mixed-anion dichalcogenides [e.g. $Mo(S,Se)_2$].[38]

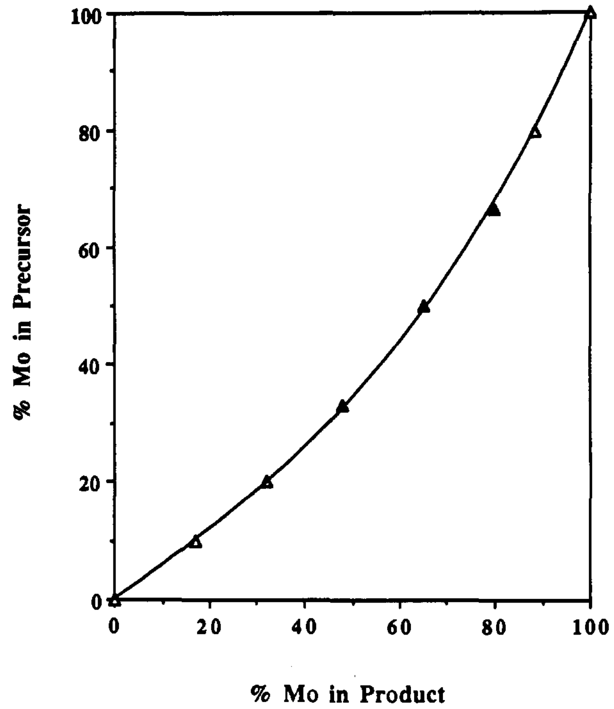

Figure 3. Stoichiometric relationship between various molybdenum tungsten chloride precursors and the products of their reactions with sodium monosulfide. The curve is a third-order polynomial fit of calculated data (open triangles) with overlayed experimental data (solid triangles). The polynomial equation has the form $y = -0.0455 + 0.581x - 6.79 \times 10^{-5}x^2 + 4.26 \times 10^{-5}x^3$.

Conclusions

Reactions between mixed molecular metal halides and alkali-metal chalcogenides rapidly produce group V and group VI mixed-metal dichalcogenides. The group VI metal dichalcogenide samples can be reduced by hydrogen to the corresponding refractory alloys. Powder X-ray analyses of several Mo–W alloys qualitatively reveal that the precursor preparations yield metal distributions in the metal dichalcogenides that are equal to or superior to the metal homogeneity in $(Mo,W)S_2$ samples produced in reactions between the elements at 1000 °C for 4 weeks. Solid-state precursor reactions are an extremely efficient alternative to traditional high-temperature reactions and an attractive route to high-quality, solid-solution compounds.

Acknowledgment. We thank Professor C. N. J. Wagner for many helpful discussions and for use of his excellent X-ray diffraction facilities. This work was supported by the National Science Foundation, a David and Lucile Packard Foundation Fellowship in Science and Engineering, and a Dreyfus Teacher-Scholar Award.

---

(36) Mesnage, P. *C. R. Acad. Sci.* **1939**, *208*, 1721.

(37) Sands, D. E.; Zalkin, A. *Acta Crystallogr.* **1959**, *12*, 723.

(38) Bonneau, P. R.; Kaner, R. B. *Inorg. Chem.* **1992**, *31*, 2127.