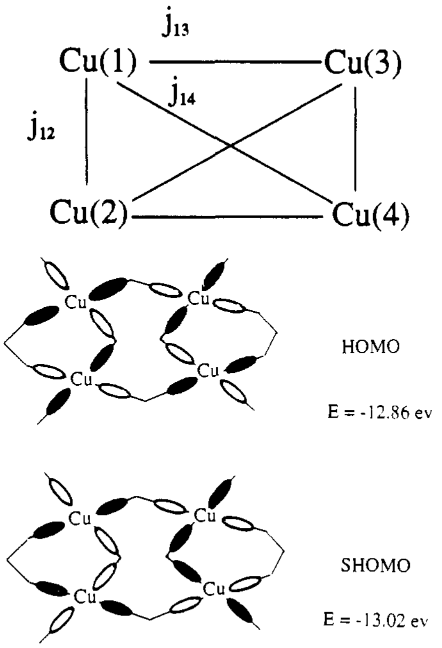

Figure 9. (a, Top) theoretical fitting model. (b, Bottom) d orbitals of Cu atoms in the HOMO and SHOMO.

this system has not been understood. The magnetic susceptibility has a minimum at about 27 K. After this temperature it steadily increases. The magnetic susceptibility at a low temperature range appears to be dominated by antiferromagnetism. A rectangular model (Figure 9a) with three j coupling constants, $j_{12} = j_{34}$, $j_{23} = j_{14}$, $j_{13} = j_{24}$, was used to fit the experimental data. The general magnetic susceptibility expression derived by Hatfield and coworkers from the Van Vleck equation for a tetranuclear Cu(II) complex[23] was used for the theoretical fitting. The data were corrected for temperature-independent paramagnetism (TIP), the presence of paramagnetic monomer impurity, and diamagnetism according to eq 4. The best fitting for the data at 0.5 kG (Figure 8b) yielded the values $g = 2.19$, $j_{12} = -186.5$ cm^{-1}, $j_{23} = 39.7$ cm^{-1} and $j_{13} = -4.4$ cm^{-1}. These results suggest that the electron-spin exchange in this system appears to be dominated by this coupling. The large antiferromagnetic exchange constant j_{12} could be attributed to the spin exchange between Cu(1) and Cu(2) bridged by an acetate ligand and a hydroxy ligand, since the Cu(1)–Cu(2) separation is the shortest compared with other Cu–Cu distances in **3** and antiferromagnetic couplings of electron spins are most common among dinuclear Cu(II) complexes with similar ligand environments.[12,24] The smallest exchange constant j_{13} can be assigned to the spin exchange of Cu(1) and Cu(1′), since this pair of Cu(II) ions is more than 4 Å apart. As a result of such assignment, the spin exchange between Cu(1) and Cu(2′) is ferromagnetic. Ferromagnetic exchanges between dimers in dimer–dimer types of tetranuclear copper(II) complexes have been observed previously.[23,24]

$$\chi_{\mathrm{calc}} = (1 - \rho)\chi + \chi_{\mathrm{TIP}} + \rho\chi_{\mathrm{mono}} + \chi_{\mathrm{diam}} \qquad (4)$$

$$\rho = 1.067 \times 10^{-3}$$

$$\chi_{\mathrm{TIP}} = 9.181 \times 10^{-4}$$

χ_{mono} = molar susceptibility of monomeric cupric impurity

$$R = 0.777 \times 10^{-2}$$

The results of MO calculations indicate that about 20% of the contributions are from copper atomic orbitals in the HOMO and second HOMO which are mainly $d_{x^2-y^2}$ in character, as shown in Figure 9b. The HOMO and SHOMO are close in energy. The electron-spin couplings in this molecule are probably through these σ orbitals.

Conclusion. A new class of cyclic tetranuclear Cu(II) complexes has been synthesized. These complexes are capable of forming one-dimensional arrays in the solid state if appropriate ligands and metal ions are present. They are potential precursors for the syntheses of heteronuclear metal complexes with compositions and structures resembling those of high-T_c superconductors. Compound **3** displays interesting field-dependent behavior in magnetic susceptibility. Further investigation on this behavior is necessary in order to have a full understanding of the magnetic property in this system.

Acknowledgment. We thank the University of Windsor and the Natural Science and Engineering Research Council for financial support.

Supplementary Material Available: Table S1, listing crystallographic data for **1**–**4**, Tables S2–S7 and S10–S12, giving H atom parameters, anisotropic temperature factors, and bond lengths and angles of the PF_6 anions for **1**, **2**, and **4**, Tables S8 and S9, giving H atom parameters and anisotropic temperature factors for **3**, Tables S21–S22, listing bond lengths and angles for the dmap ligand and CH_2Cl_2 molecule in **1** and **4**, and Figures S17–S20, showing the structures of the CH_2Cl_2 solvent molecule and the PF_6 anion in **1** and **4** (24 pages); Tables S13–S16, listing observed and calculated structure factors for **1**–**4** (61 pages). Ordering information is given on any current masthead page.

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Solid-State Metathesis as a Quick Route to Transition-Metal Mixed Dichalcogenides

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Solid-solution transition-metal dichalcogenides, traditionally synthesized from the elements at elevated temperatures over long periods of time, can now be prepared from rapid self-propagating reactions between transition-metal halides and alkali-metal mixed chalcogenides such as $Na_2(S,Se)$. The transition-metal dichalcogenide solid solution is isolated by simply washing away the byproduct salt. Powder X-ray diffraction and thermogravimetric analyses of the solid solutions $Mo(S,Se)_2$ and $W(S,Se)_2$ are presented. Although any composition can theoretically be prepared, the stoichiometry of the product is influenced by the temperatures attained during the course of the reaction. The products are characteristically enriched in the more volatile non-metal component relative to the alkali-metal mixed-chalcogenide precursor. The observed kinetic products and selective enrichment suggest that elemental intermediates may be involved in these reactions.

Introduction

Precursor reactions are an effective synthetic route for the preparation of a large number of materials. One type of precursor method involves an exchange of two or more species during a reaction. Reactions of this type can, in principle, be carried out in the liquid, gas, or solid state.[1-5] The approach, however, has

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not been fully explored as a solid-state synthetic technique, especially with respect to the preparation of solid-solution compounds.

Layered transition-metal dichalcogenides are an important class of materials which have been the focus of numerous studies over the past three decades because of their diverse applications as industrial lubricants,[6] battery cathodes,[7,8] and hydrodesulfurization catalysts.[9] They form a wide range of solid solutions with either mixed-metal or mixed-anion compositions.[10–13] The solid-solution compounds have been targeted for extensive study of structural and electronic or magnetic property changes as a function of composition.[13–16]

Layered transition-metal mixed dichalcogenides, $M(S,Se)_2$ or $M(Se,Te)_2$, are generally prepared by heating their constituent elements at elevated temperatures for prolonged periods.[10] Metal halide salts, either as solids or in solution, will react with binary alkali-metal chalcogenides[17] or organic chalcogeniding agents [e.g. $((CH_3)_3Si)_2S$][18] to yield binary dichalcogenides, yet these precursors have not been used to prepare ternary compounds. Reactions between transition-metal halides and mixtures of chalcogenide gases (H_2S, H_2Se, or H_2Te) or organic chalcogenide agents could also be used in the preparation of ternary compounds; however, these would pose synthetic difficulties due to differences in vapor pressures and high toxicities. Alkali-metal chalcogenide solid solutions such as $Na_2(S,Se)$ or $Na_2(Se,Te)$, on the other hand, can be easily synthesized, safely manipulated, and reacted with many transition-metal halides, providing a convenient route to mixed-anion transition-metal dichalcogenides.

Solid-state precursor reactions between transition-metal halides and alkali-metal chalcogenides initiate at relatively low temperatures and are extremely rapid, often on the order of 1–5 s.[19] The frequently self-propagating and sometimes explosive behavior of these reactions can be attributed to the heats they generate (100–250 kcal/mol). Some of the reactions attain temperatures of 1000 °C or more, liquefying or vaporizing most of the reagents and products. Under these circumstances, solid-state diffusion is no longer rate-limiting and the rate of reaction becomes sufficiently rapid to overwhelm the rate of heat dissipation. Similar reaction conditions have been described for other self-propagating solid-state reactions.[20–22] Consequently, intense flashes of light and "mushroom clouds" of volatile species are often observed. The result is generally a dark, fused mass containing the transition-metal dichalcogenide product and alkali-metal halide byproduct. The desired product is most often isolated by simply washing away the soluble byproducts.

Two techniques for carrying out solid-state precursor reactions involve ignition of the reactant mixture with a hot filament in a stainless-steel bomb or reaction in a sealed quartz tube under prolonged heating conditions.[23] Ignition of the reactant mixture in bombs takes advantage of the very exothermic nature of the precursor reactions. A brief and very intense local heat caused by the filament initiates the process, and the reaction then proceeds spontaneously through the bulk of the mixture. Another characteristic of this method is that the temperatures attained are dependent upon the nature and the amount of the precursors used. Most reactions proceed on a relatively short time scale. Within seconds, the reaction achieves its maximum temperature and is then virtually quenched. The slower and more energy consumptive reactions carried out in sealed tubes are usually more efficient in terms of product yield, and they invariably lead to thermodynamic products.

The goal of this research is to develop precursor routes to transition-metal mixed-anion solid solutions. This work deals with the preparation of molybdenum and tungsten mixed-anion dichalcogenides by ignition of molybdenum pentachloride or tungsten hexachloride and an alkali-metal mixed-chalcogenide salt. Since these reactions cool almost as quickly as they ignite, some of the products observed are not thermodynamic and others do not necessarily reflect the stoichiometry of the non-metals in the alkali-metal mixed-chalcogenide reactants. Explanations of the observed kinetic phases and selectively-enriched products are offered.

Experimental Section

The preparation and treatment of precursors play a crucial role in determining the reaction conditions and the product yield in solid-state exchange reactions.[19,23] Transition-metal halides are therefore resublimed to remove the highly volatile metal oxychloride contaminants and to separate the monomeric halides from the less-volatile, lower-valent metal(III, IV) halides. This procedure leads to higher reaction yields as well as, in some cases, lower initiation temperatures and more crystalline products. In addition, alkali-metal chalcogenide reagents are sintered in order to prevent spontaneous ignition of reaction mixtures containing molecular transition-metal halide precursors. The reactants can then be combined and reacted more conveniently in a stainless-steel bomb.

Molybdenum pentachloride (Johnson Matthey/Aesar, 99.6%) and tungsten hexachloride (Johnson Matthey/Aesar) were purified by resublimation in an evacuated, sealed glass tube (25 mm o.d. × 25 cm) placed in a 250 °C–room-temperature gradient. The alkali-metal mixed-chalcogenide precursors, $Na_2(S,Se)$ and $Na_2(Se,Te)$, were prepared by reacting a stoichiometric amount of the elements (placed in a single-chamber thick-wall Pyrex reactor tube while in a He atmosphere) in liquid ammonia.[24] When the reaction was complete, the ammonia was allowed to evaporate and the poorly crystalline material was sintered at 500–600 °C for 12 h. The alkali-metal mixed-chalcogenide reagents can also be synthesized by mixing appropriate amounts of the unsintered binaries (precipitated from liquid ammonia) and by heating the mixture at 500–600 °C in a silica tube for 2 days.

Reactions between the above reagents are very exothermic and sometimes explosive. Since these reactions can self-ignite, especially in the presence of moisture, the reactions are typically carried out under inert atmosphere in covered, loosely sealed bombs in order to contain the fulminating mixtures. The precursors are potentially hazardous. On exposure to air or on washing with water, the product mixtures can evolve toxic gases from some of the unreacted starting materials, i.e. H_2S and HCl from Na_2S and $MoCl_5$, respectively. Workups should, at a minimum, be done in a fume hood. Incomplete reactions can sometimes be a problem. If unreacted materials are present in the reaction mixture, the addition of solvent can promote further reaction. This is potentially hazardous, since the heat of the reaction is often sufficient to ignite flammable solvents such as methanol.

In a He-filled glovebox, the purified transition-metal halides and the sintered alkali-metal chalcogenide solid solutions were ground separately, combined, and placed into a stainless-steel bomb (50-mm height, 48-mm o.d., 35-mm i.d.) similar to those used in calorimetry experiments.[25] Typically, 0.750 g of metal chloride ($MoCl_5$ or WCl_6) was mixed with 0.697 g or 0.576 g of $Na_2S_{0.5}Se_{0.5}$, respectively. The mixture of starting reagents was then ignited with a heated filament, which started a self-

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Table I. Summary of Syntheses for Binary Materials

reactant mixture	method	products[a]
$MoCl_5 + {}^5/_2Na_2S$[b]	self-ignition in mortar after mixing 10–15 s	$MoS_2 + NaCl + S$ + trace Mo
$MoCl_5 + {}^5/_2Na_2S$	bomb ignition	$MoS_2 + NaCl + S$
$WCl_6 + 3Na_2S$	bomb ignition	$WS_2 + NaCl + S$
$MoCl_5 + {}^5/_2Na_2Se$	bomb ignition	$MoSe_2 + NaCl + Se$
$WCl_6 + 3Na_2Se$	bomb ignition	$WSe_2 + NaCl + Se$
$MoCl_5 + {}^5/_2Na_2Te$	bomb ignition	$Mo_3Te_4 + NaCl + Te$ + trace $MoTe_2$ and Mo
$WCl_6 + 3Na_2Te$	bomb ignition	$W + Te + NaCl$ + trace WTe_2
$MoCl_5 + {}^5/_2Na_2Te$	evacuated quartz tube at 1000 °C for 7 days	$MoTe_2 + NaCl + Te$
$WCl_6 + 3Na_2Te$	evacuated quartz tube at 1000 °C for 7 days	$WTe_2 + NaCl + Te$

[a] Before workup. [b] Unsintered Na_2S; self-ignition occurs in any reaction containing unsintered alkali-metal chalcogenide reagent.

propagating and very exothermic reaction. Initial calculations based upon Hess's law and heat capacities of the products predict that these reactions should reach the boiling point of the salt produced (in these cases, NaCl bp = 1413 °C). Optical pyrometry measurements, in fact, showed that the MoS_2 reaction reaches at least 1050 °C.[19] The product, a gray fused mass, was ground in the glovebox, removed, and washed with water, methanol, and ether. Residual sulfur and selenium were removed by heating the product with a heat gun while it was drying on a vacuum line. Since reactions with sodium telluride produced large amounts of tellurium and other relatively insoluble and nonvolatile phases, the reaction products were not purified.

The high-temperature control reactions for the binary tellurides were carried out in flame-dried quartz tubes loaded with reactant mixture in a He-filled drybox. The quartz tubes were placed on a vacuum line and the samples cooled with liquid nitrogen before evacuation to prevent spontaneous ignition and loss of volatile reagents while the samples were exposed to vacuum. The quartz tubes were then evacuated, sealed, and placed in a furnace, where they were heated at 1000 °C for 7 days. The cooled samples were isolated by washing with water and methanol and dried on a vacuum line.

Powder X-ray diffraction patterns were obtained using a GE powder diffractometer with Ni-filtered Cu Kα radiation. The scans were carried out in steps of 0.05° 2θ at a rate of 5 s/step. The stoichiometries of the transition-metal dichalcogenide solid solutions were determined by thermogravimetric analysis, TGA (Du Pont 9900 Thermal Analysis System), and verified by elemental analysis (Galbraith Laboratories, Inc., Knoxville, TN). In TGA experiments, the solid solutions were reduced under a 5% H_2/95% N_2 atmosphere at 900–950 °C until no further weight loss occurred (approximately 50 h). The TGA residues were examined by powder X-ray diffraction and found to be pure Mo or W metal.

Results

The new alkali-metal mixed-anion chalcogenides, $Na_2(S,Se)$ and $Na_2(Se,Te)$, like Na_2S, Na_2Se, and Na_2Te, are easily synthesized in virtually any composition and can be more safely manipulated than the highly volatile and extremely toxic chalcogenide gases. The solid-solution compounds, also like the binaries, crystallize in the cubic antifluorite structure. The stoichiometries of several alkali-metal chalcogenide precursors and their respective lattice parameters are plotted in Figure 1. The plots reflect a linear increase in the cubic lattice parameter *a* as the concentration of the larger anion increases. Although high-quality $Na_2(S,Se)$ and $Na_2(Se,Te)$ are readily accessible, the coprecipitation of Na_2S and Na_2Te, on the other hand, produced phase-segregated components rather than the desired $Na_2(S,Te)$.

The reactions carried out in this study are shown in Tables I and II. Table I summarizes the reactions between group VI transition-metal chlorides and binary alkali-metal chalcogenides, the reaction conditions, and the products of the reactions before washing. Bomb ignition reactions involving S and Se produce metal dichalcogenides, while those reactions involving Te yield only trace amounts of dichalcogenide. Metal ditellurides were, however, produced in tube reactions at 1000 °C for 7 days.

Reactions of the type

$$MCl_x + (x/2)Na_2(S,Se) \rightarrow M(S,Se)_2 + xNaCl + (x/2 - 2)(S,Se) \quad (1)$$

where M = Mo or W and x = 5 or 6, are very exothermic (>170 kcal/mol) and yield good ternary materials in just seconds. Thermogravimetric analyses of several $Mo(S,Se)_2$ and $W(S,Se)_2$ products prepared from the indicated transition-metal halides and alkali-metal mixed chalcogenides are presented in Table II. Here it can be seen that all of the products are enriched in sulfur over selenium compared to the predicted stoichiometry of product.

Table II. Ternary Systems: Reactant and Product Stoichiometries

metal halide reagent	alkali-metal chalcogenide	theor stoichiom of product	TGA of product
$MoCl_5$	$Na_2S_{0.25}Se_{0.75}$	$MoS_{0.50}Se_{1.50}$	$MoS_{0.72}Se_{1.28}$
	$Na_2S_{0.50}Se_{0.50}$	$MoS_{1.00}Se_{1.00}$	$MoS_{1.20}Se_{0.80}$
			$MoS_{1.19}Se_{0.81}$
			$MoS_{1.11}Se_{0.89}$
	$Na_2S_{0.75}Se_{0.25}$	$MoS_{1.50}Se_{0.50}$	$MoS_{1.74}Se_{0.26}$
WCl_6	$Na_2S_{0.25}Se_{0.75}$	$WS_{0.50}Se_{1.50}$	$WS_{0.71}Se_{1.29}$
	$Na_2S_{0.50}Se_{0.50}$	$WS_{1.00}Se_{1.00}$	$WS_{1.03}Se_{0.97}$
	$Na_2S_{0.75}Se_{0.25}$	$WS_{1.50}Se_{0.50}$	$WS_{1.60}Se_{0.40}$

The powder X-ray diffraction patterns for a series of MoS_2, $Mo(S,Se)_2$, and $MoSe_2$, shown in Figure 2, illustrate the progression of selected diffraction peaks to lower angles as the concentration of selenium increases. The analogous precursor reactions between $MoCl_5$ and $Na_2(Se,Te)$ do not produce a similarly wide range of molybdenum selenide–telluride solid solutions. They generally yield phase-segregated products, among those $Mo(Se,Te)_2$ containing only a few mole percent Te with respect to the total amount of chalcogenide and excess Te (Figure 3).

Discussion

Self-propagating, solid-state reactions between molybdenum pentachloride or tungsten hexachloride and sodium sulfide selenide represent a fresh approach to the preparation of transition-metal mixed dichalcogenides. Additionally, solid-state precursor reactions producing solid-solution dichalcogenides introduce several intriguing results which make them interesting from a mechanistic point of view. Most noteworthy are the change in the ratio of the non-metals from precursor to product, the presence of a compositional gradient in the product, and a dependence of the product stoichiometry on the amount of reagents used. With respect to the latter point, smaller amounts of reagents usually favor the enrichment of the more volatile chalcogen in the product. The above observations, as will be seen, are entirely consistent with a mechanistic model that includes elemental intermediates. Since the results of certain reactions producing binary dichalcogenides are useful for the understanding and interpretation of the peculiarities encountered in ternary systems, this section must include a brief discussion of binary systems.

Binaries. Previous experiments with rapid, solid-state syntheses of transition-metal dichalcogenides revealed that mixtures of molybdenum pentachloride and unsintered sodium monosulfide generally self-ignite before the reactants can be properly mixed. Among the expected products of molybdenum disulfide, sodium chloride, and excess sulfur, a small amount of elemental molybdenum was invariably detected (Table I). The analogous reaction containing sintered sodium monosulfide, on the other hand, did not prematurely self-ignite and did not produce any molybdenum metal. Only later was the importance of reagent particle size with respect to self-ignition and product formation determined. In systems where spontaneous ignition was not a problem, the reagents were intimately mixed and the result was generally an increase in the yield of desired product. In systems where self-ignition occurred with a finely-divided alkali-metal chalcogenide reagent, the reagents could be sintered to suppress premature

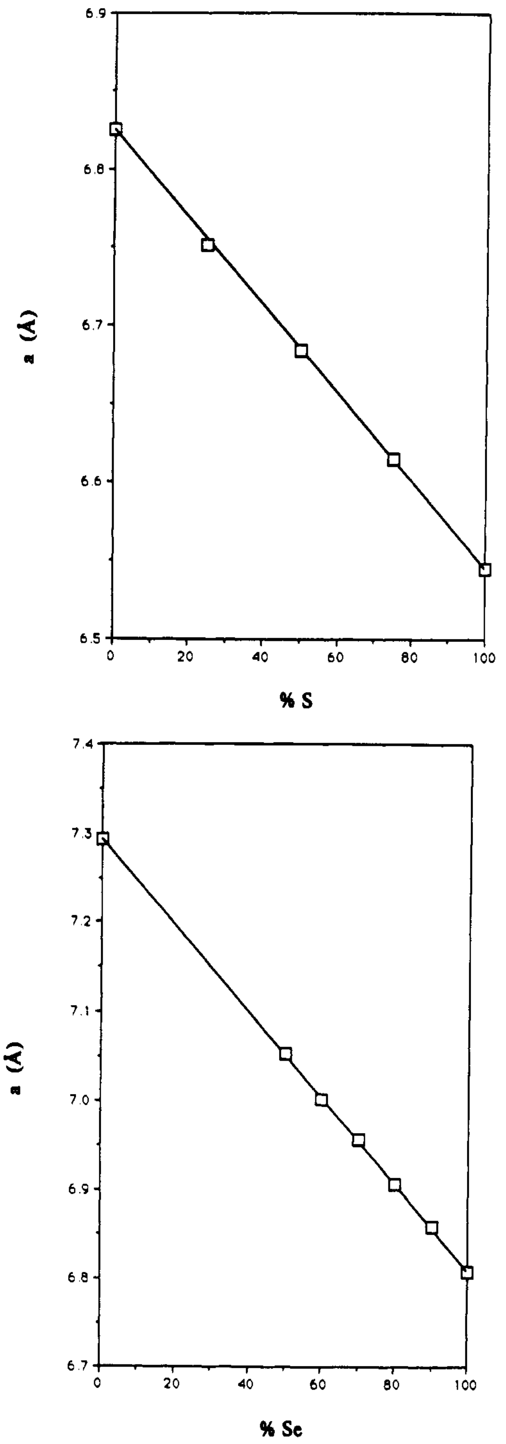

Figure 1. Top: Plot of cubic lattice parameter *a* versus percent S in the solid-solution reagent $Na_2S_xSe_{1-x}$. Bottom: Plot of cubic lattice parameter *a* versus percent Se in the solid-solution reagent $Na_2Se_xTe_{1-x}$. Both plots include lines connecting the points representing the two binaries. The lattice constants for the ternary chalcogenides change linearly with composition, as expected for solid-solution compounds exhibiting Vegard law behavior.

ignition and associated metal formation.

Another peculiarity was discovered when this synthetic approach was applied to the preparation of binary tellurides (Table I). Although $MoCl_5$ or WCl_6 reacts with Na_2X (X = S or Se) to form pure MoS_2, $MoSe_2$, WS_2, or WSe_2,[19] respectively, the analogous reactions between $MoCl_5$ or WCl_6 and Na_2Te do not produce the expected transition-metal ditellurides. Only traces of $MoTe_2$ and WTe_2 are observed. The idealized reactions are

$$MoCl_5 + \tfrac{5}{2}Na_2Te \rightarrow \tfrac{1}{3}Mo_3Te_4 + 5NaCl + \tfrac{7}{6}Te \qquad (2)$$

$$WCl_6 + 3Na_2Te \rightarrow W + 6NaCl + 3Te \qquad (3)$$

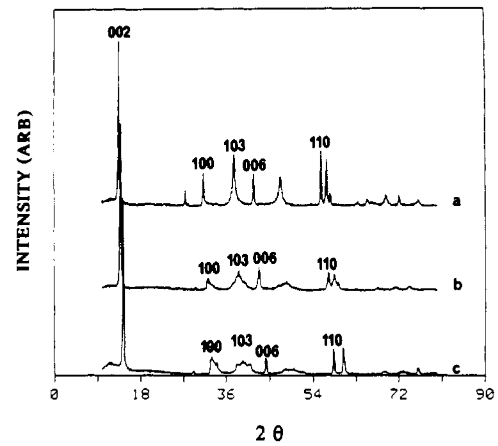

Figure 2. Powder X-ray diffraction patterns of the polycrystalline products formed in the reactions between $MoCl_5$ and Na_2Se, $Na_2S_{0.5}Se_{0.5}$, or Na_2S: (a) $MoSe_2$; (b) $Mo(S,Se)_2$; (c) MoS_2, respectively. The selectively labeled peaks illustrate the evolution of diffraction lines to higher angles as the concentration of the smaller anion increases.

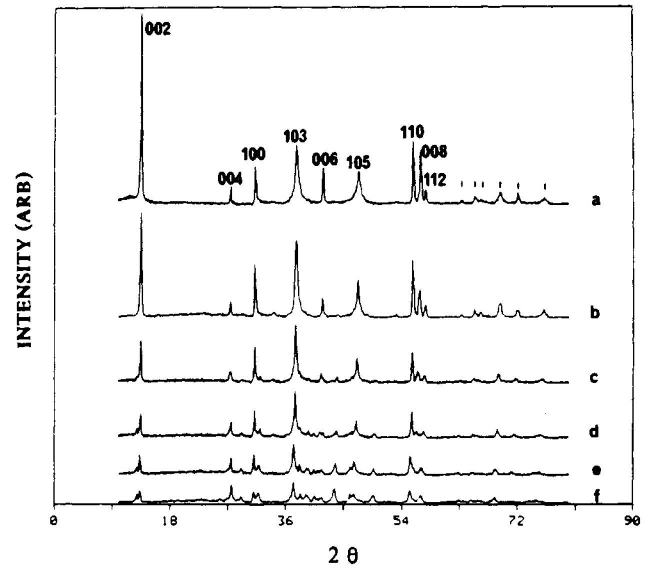

Figure 3. Powder X-ray diffraction patterns of the product(s) of the reactions between $MoCl_5$ and (a) Na_2Se, (b) $Na_2Se_{0.9}Te_{0.1}$, (c) $Na_2Se_{0.8}Te_{0.2}$, (d) $Na_2Se_{0.7}Te_{0.3}$, (e) $Na_2Se_{0.6}Te_{0.4}$, and (f) $Na_2Se_{0.5}Te_{0.5}$. The Miller indices for pure $MoSe_2$, shown in (a), occurring beyond 63° (2θ) are 114, 200, 108, 203, 116, and 205, respectively.

The heats of formation, ΔH_f's, for Mo_3Te_4 and α-$MoTe_2$ are −193 and −91.1 kJ/mol, respectively.[26] The thermodynamic product in reaction 2, after normalizing for molybdenum content, should therefore be molybdenum ditelluride. The thermodynamic phase in reaction 3 should likewise be WTe_2.[27] Since both $MoTe_2$ and WTe_2 can be prepared from the elements at temperatures as high as 1000–1200 °C,[10] it is unlikely that the temperatures generated in the precursor reactions decompose the product.

High-temperature reactions clearly demonstrate that the elements formed in the ignited precursor reactions are indeed kinetic, rather than thermodynamic, phases. When molybdenum pentachloride or tungsten hexachloride is combined with a stoichiometric amount of sodium telluride in an evacuated, sealed quartz tube which is then heated at 1000 °C for 1 week, the products are molybdenum or tungsten ditelluride, excess tellurium, and sodium chloride (Table I). These results confirm that the expected thermodynamic products do form, even in the presence of the sodium chloride flux, provided that the elements are given sufficient time to react at sustained, elevated temperatures.

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Under conditions of poor reagent mixing and short reaction times at high temperatures, the presence of transition metals and chalcogen as elemental species in the product mixtures may be a strong indication of the pathway in these reactions. If the formation of sodium chloride, usually the driving force in these reactions, is a very large portion of the total enthalpy of reaction, then sodium may relatively easily strip the halide ligands from the metal cations, leaving the highly charged ions in a sodium chloride flux. The large difference in oxidation state between the cationic and anionic species favors a very strong redox process leading to the formation of elements, especially since alkali-metal halide fluxes do not appear to easily stabilize charged species.[28] The elements would then have to rely on the heat generated by the preceding processes for diffusion and product formation. It is reasonable to assume that, in these extremely rapid reactions where the maximum temperature is not sustained for more than a few seconds, favorable thermodynamic conditions are not maintained sufficiently long for the elements to completely react. This would be especially true in systems where both the metal and the non-metal have relatively low vapor pressures, i.e. molybdenum or tungsten and tellurium. If this is indeed the case, then the elements can be considered as "quenched" intermediates or kinetic products.

Ternaries. Following the success with group VI transition-metal disulfides and diselenides, our attention focused on transition-metal mixed dichalcogenides. The preparation of ternary dichalcogenides by the solid-state precursor method is as straightforward as the synthesis of the binary materials, since only a slight modification is necessary. The binary alkali-metal chalcogenide reagent is simply replaced by an alkali-metal mixed-anion chalcogenide.

Precursor reactions, as well as high-temperature routes from the elements,[12] can be used to prepare all compositions of the solid-solution series $Mo(S,Se)_2$. Additionally, high-temperature syntheses have been used to prepare the $Mo(Se,Te)_2$ series.[16] The precursor reactions between $MoCl_5$ and $Na_2(Se,Te)$ do not, however, yield the expected $Mo(Se,Te)_2$ products. When the alkali-metal mixed-chalcogenide precursor is $Na_2Se_{0.90}Te_{0.10}$, the product of the reaction with $MoCl_5$ is essentially molybdenum diselenide with less than 2 mol % Te with respect to the total amount of chalcogen. When alkali-metal chalcogenide solid solutions containing greater than 10 mol % Te are used, the appearance of other phases becomes quite evident (Figure 3). This outcome is not entirely unexpected, considering the results of experiments with binary dichalcogenides.

Before experimental results with the binary sulfide and telluride reactions suggested the possibility of elemental intermediates, selective enrichment of the more volatile chalcogen in the product and its dependence on the amount of reagents used were very difficult to fully explain strictly from the point of view of redox potentials or an ion-exchange mechanism. The preferential oxidation of the more metallic chalcogenide species can account for selective enrichment, but it does not satisfactorily explain how smaller amounts of reagents favor enrichment of the more volatile non-metal in the product.

In all reactions between molybdenum pentachloride or tungsten hexachloride and sodium mixed chalcogenides, the ratio of the non-metals varies from precursor to product. When sulfide–selenide reagents are used, the product is slightly enriched in sulfur (Table II); when selenide–telluride reagents are used, the product is drastically enriched in selenium. If the observed elemental species in these reactions are indeed quenched intermediates, then it is only reasonable that the physical properties of the constituent elements under these conditions should be important. Molybdenum and tungsten, from the reduction of molybdenum pentachloride and tungsten hexachloride, are refractory metals and immobile relative to the volatile non-metals. Under normal reaction conditions of extremely rapid heating and only slightly slower cooling, the non-metals compete with each other for reaction with the metal. Sulfur (bp 445 °C) maintains a higher vapor pressure longer than selenium (bp 680 °C), and both of these maintain their vapor pressures much longer than tellurium (bp 1390 °C). Sulfur and selenium throughout most of the reaction are gases, while Te (mp 452 °C) is a liquid. The gaseous nonmetals have a much higher mobility than the elements in condensed phases and, therefore, are better able to quickly diffuse to a reaction site before the flux is quenched. Hence sulfur, remaining as a gaseous species longest, enriches a bit more than selenium and selenium much more than tellurium.

A second interesting and very closely related phenomenon is the presence of a compositional gradient in the ternary compounds. This effect, readily detected by powder X-ray diffraction, can be seen in Figure 2. The molybdenum sulfide selenide samples generally exhibit broadened X-ray lines relative to MoS_2 and $MoSe_2$ prepared under identical conditions. This can be seen by comparing the 110 lines, and to a lesser extent the 00*l* lines such as 006. Any broadening due to particle size or poor interlayer registry should therefore be comparable in all samples. Another factor often responsible for line broadening is a compositional gradient, or localized variation in product stoichiometry. X-ray diffraction peaks, normally quite narrow if they originate from a uniform set of *d* spacings in well-crystallized, homogeneous samples, become "envelopes" of lines, each representing slightly different *d* spacings in inhomogeneous sample crystallites. Elemental sulfur and selenium at the elevated reaction temperatures are gases and are not limited to solid-state diffusion. Once again, sulfur, possessing the higher vapor pressure, is able to diffuse more rapidly to the reactive metal sites. Consequently, any given region of a single particle would likely contain a nonstatistical distribution of sulfur and selenium, or a compositional gradient.

Finally, the factors responsible for preferential enrichment and a compositional gradient in the product make exact control of product stoichiometry difficult. In three separate reactions where only the total amount of reagents varied (from 1.45 to 1.93 g), molybdenum pentachloride reacted with $NaS_{0.50}Se_{0.50}$ (calculated from lattice parameter measurements and verified as $NaS_{0.49}Se_{0.50}$ by elemental analysis) to form three different products with an average stoichiometry of $MoS_{1.14}Se_{0.86\pm0.06}$. Since the vapor pressures of the non-metals, sulfur and selenium, and their ability to diffuse and react with molybdenum are influenced by the temperatures of the reaction, the amount of reactants used can significantly affect product stoichiometry. The larger the reacting mass, the more insulated the bulk and the higher the temperature generated within the flux. The temperatures attained throughout all phases of the reaction then influence the vapor pressures, diffusion, and reaction of the competing non-metals.

Of all aspects of self-sustaining precursor reactions including initiation and kinetic product formation, the mechanistic steps involved in propagation are the least understood. Because of the inherently rapid nature of propagation in these systems, chemical methods are ineffectual for the study of the changes in the intermediate species after initiation and before the formation of quenched species. The rapid propagation, however, most often generates a high-temperature, light-emitting flux. Spectroscopic studies of these radiant emissions could provide more information about the intermediates involved in this process and, therefore, a better understanding of self-sustaining reactions in general.

Solid-state precursor reactions are very effective for the synthesis of many binary materials. Additionally, simple substitution of the alkali-metal chalcogenide reagent with an alkali-metal mixed chalcogenide in these reactions leads to good molybdenum and tungsten sulfide selenides. Some minor improvements, however, would make solid-solution-precursor reactions a more viable synthetic technique for ternary materials in general. The changes include: the use of reagents which react stoichiometrically, not only with respect to the formation of the alkali-metal halide salt but also with respect to the formation of the product, i.e.

$$MCl_4 + 2Na_2(S,Se) \rightarrow M(S,Se)_2 + 4NaCl \qquad (4)$$

and slightly longer heating times at moderate temperatures. Reactions carried out in evacuated, sealed tubes at elevated temperatures for prolonged periods often yield thermodynamic,

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not kinetic, phases. In the case of stoichiometric reactions, the thermodynamic product forcibly has the same stoichiometry as the ternary reagent, since the product lattices are so much more energetically favorable than the reagent lattices. In nonstoichiometric reactions like (1), free non-metal byproducts are also produced, and their presence is a complication. The different volatilities of S and Se, not only in the solid-solution product but also from the free elements, bring about changes in the composition of the final product at different temperatures. The final product is therefore dependent upon the relative bond strengths between the metal and the competing non-metal components, their volatilities, and the thermal treatment of the reaction once it has reached equilibrium at a specific temperature and pressure. The study of a solid-gas equilibrium for such a system is a formidable task. The above modifications therefore address the problems associated with the presence of excess chalcogen and the unequal diffusion rates of competing non-metals leading to preferential enrichment, compositional gradients, and variable stoichiometry.

The solid-state, solid-solution-precursor approach is also applicable to other mixed-anion systems. Experiments with metal mixed-pnictide and metal chalcogenide/pnictide systems are in progress. Alkali-metal mixed pnictides, such as $Na_3(P,As)$ and $Na_3(As,Sb)$, are prepared by heating their constituent elements at moderate temperatures. Like their mixed-chalcogenide analogues, they can be more safely manipulated than the corresponding gases, phosphine or arsine. They are then reacted with a large number of main-group and rare-earth metals to produce compounds such as Ga(P,As) or Gd(P,As).[29]

Conclusions

Experiments with binary group VI transition-metal dichalcogenides illustrate that part of the mechanism in these self-sustaining, solid-state precursor reactions appears to involve elemental intermediates that are the result of a powerful redox process. The high reaction temperatures generated promote reaction between the elements to form product. As is the case with most solid-state reactions, diffusion is a very important consideration. Any factors favoring diffusion, such as smaller reagent particle sizes or more intimate mixing, higher temperatures, and longer heating times, also favor products. The proposed mechanistic arguments are further supported by experiments with molybdenum and tungsten mixed-anion dichalcogenides. The phenomena of selective enrichment, compositional gradients, and variable stoichiometry in the products are readily explained by the competitive diffusion of different non-metals under reaction conditions of rapid, nonuniform heating and quick cooling.

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Contribution from the Dipartimento di Chimica, Università di Firenze, and Istituto per lo Studio della Stereochemica ed Energetica dei Composti di Coordinazione, Firenze, Italy

Electronic Structure and Magnetic Properties of the Hexanuclear Octahedral Cluster $[Co_6(\mu_3\text{-}S)_8(PEt_3)_6]BPh_4$

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Single-crystal EPR spectra of the paramagnetic complex $[Co_6(\mu_3\text{-}S)_8(PEt_3)_6]BPh_4$ (PEt_3 = triethylphosphine; BPh_4 = tetraphenylborato anion) at 4.2 K were interpreted using a $S = {}^1/_2$ spin Hamiltonian with $g_x = 2.35$ (1), $g_y = 2.04$ (1), and $g_z = 1.95$ (1). The x, y, and z axes are close to the bond directions of one of the six inequivalent cobalt atoms. The compound is EPR silent at room temperature, both in the solid state and in solution. The temperature dependence of the intensity of the EPR signal is ascribed to a localization of the unpaired electron on one cobalt nucleus. The angular dependence of the peak-to-peak line width of the 4.2 K EPR signal seems to indicate the existence of a feeble magnetic interaction between the clusters in the solid state.

Introduction

Oligonuclear complexes of transition metals have attracted the interest of the scientific community for a long time, since they form the natural union between molecular and solid-state chemistry.[1] Agglomerates of metals have been found in naturally occurring enzymes, such the iron-sulfur proteins, as well as in pure inorganic solids,[2] and a large part of inorganic chemistry has recently been devoted to the synthesis of new types of clusters and to the development of theoretical methods for the calculation of their electronic structure.[3] Sulfide-containing minerals probably represent the best known naturally occurring inorganic systems in which aggregates of metals are present.[4] Some of these minerals offer peculiar physical properties arising from the fact that the metal-sulfur clusters are extensively interconnected to form extended structures. The best known substances of this type are probably the Chevrel phases of the molybdenum chalcogenides,[5] which include high-temperature and high-field superconductors.[6,7] The core of these solids is formed by a Mo_6X_8 (X = S, Se, Te, halogen) cluster in which an octahedron of six molybdenum atoms is encased in a cube of X atoms, and their electronic structure has been widely described using extended Hückel (EH) calculations.[8]

S.M. has reported the synthesis and the crystallographic characterization of a series of complexes of general formula $[M_6(\mu_3\text{-}S)_8(PEt_3)_6]^{n+}$, where M is cobalt or iron and n ranges from

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