amine intercalation.[3] However, we should note that for large molecules kinetic rather than thermodynamic considerations may dominate. We have shown that this can be important for the direct reaction for both $(\eta\text{-}C_6H_6)_2Mo$ and $(\eta\text{-}C_6H_6)_2Cr$ which do not intercalate TaS_2 by direct reaction but do so by ion exchange.

Conclusion

In summary, a wide range of organometallic molecules and cations with sandwich structures react with layered transition-metal dichalcogenides to give well-characterized crystalline intercalates. The reactions may be accomplished directly when the neutral organometallic compound acts as its own reducing agent or indirectly by ion exchange. Ion exchange is a useful technique when the kinetics of the direct reaction are slow but is generally limited by hydrolysis of the host lattice and the instability of many organometallic compounds in aqueous solution. Either ion exchange in nonaqueous solvents does not lead to intercalation or the kinetics of reaction are very slow. Electrochemical intercalations in nonaqueous media are currently being investigated as an alternative synthetic route.

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Registry No. TiS_2, 12039-13-3; ZrS_2, 12039-15-5; HfS_2, 18855-94-2; NbS_2, 12136-97-9; TaS_2, 12143-72-5; $TiSe_2$, 12067-45-7; $ZrSe_2$, 12166-47-1; VSe_2, 12299-51-3; $NbSe_2$, 12034-77-4; $TaSe_2$, 12039-55-3; $[(\eta^5\text{-}MeC_5H_4)_2Co]_{0.21}TaS_2$, 65353-19-7; $[(\eta^5\text{-}i\text{-}PrC_5H_4)_2Co]_{0.17}TaS_2$, 65254-96-8; $[(\eta^5\text{-}n\text{-}BuC_5H_4)_2Co]_{0.13}TaS_2$, 65254-97-9; $\{[(\eta^5\text{-}MeC_5H_4)_2Co]^+I^-\}_{0.14}TaS_2$, 65353-21-1; $\{[(\eta^5\text{-}i\text{-}PrC_5H_4)_2Co]^+I^-\}_{0.07}TaS_2$, 65254-99-1; $\{[(\eta^5\text{-}n\text{-}BuC_5H_4)_2Co]^+I^-\}_{0.05}TaS_2$, 65255-01-8; $\{[(\eta^6\text{-}C_6H_6)_2Cr]^+I^-\}_{0.13}TaS_2$, 65319-75-7; $\{[(\eta^6\text{-}C_6H_6)_2Mo]^+I^-\}_{0.15}TaS_2$, 65255-03-0; $\{[(\eta^5\text{-}C_5H_5)(\eta^6\text{-}C_6H_6)Fe]^+PF_6^-\}_{0.16}TaS_2$, 65255-04-1; $\{[(\eta^5\text{-}C_5H_5)_2Co]^+I^-\}_{0.20}TaS_2$, 67464-35-1; $[(\eta^5\text{-}MeC_5H_4)_2Co]_{0.25}ZrS_2$, 67464-36-2; $[(\eta^5\text{-}i\text{-}PrC_5H_4)_2Co]_{0.15}ZrS_2$, 67464-37-3; $[(\eta^5\text{-}n\text{-}BuC_5H_4)_2Co]_{0.13}ZrS_2$, 67464-38-4; $[(\eta^5\text{-}C_5H_5)_2Co]_{0.25}ZrSe_2$, 67464-39-5; $[(\eta^5\text{-}C_5H_5)_2Co]_{0.25}VSe_2$, 67464-40-8; $[(\eta^6\text{-}C_6H_6)_2Mo]_{0.16}ZrS_2$, 67464-25-9; $[(\eta^6\text{-}C_6H_6)_2Cr]_{0.16}ZrS_2$, 67464-26-0; $(\eta^5\text{-}t\text{-}BuC_5H_4)_2Co$, 59610-19-4; dimethylfulvene, 2175-91-9; $[(\eta^5\text{-}t\text{-}BuC_5H_4)_2Co]^+PF_6^-$, 67464-27-1; $[(\eta^5\text{-}i\text{-}PrC_5H_4)_2Co]^+PF_6^-$, 33635-72-2; $[(\eta^5\text{-}n\text{-}BuC_5H_4)_2Co]^+PF_6^-$, 67464-29-3; $[(\eta^6\text{-}C_6H_5CH_3)_2Mo]_{0.13}ZrS_2$, 61746-48-3; $[(\eta^6\text{-}C_6H_3(CH_3)_3)_2Mo]_{0.08}ZrS_2$, 61746-49-4; $[(\eta^5\text{-}C_5H_5)_2Cr]_{0.25}ZrS_2$, 61746-51-8; $[(\eta^6\text{-}C_6H_6)(\eta^5\text{-}C_5H_5)Cr]_{0.24}ZrS_2$, 67464-30-6; $[(\eta^7\text{-}C_7H_2)(\eta^5\text{-}C_5H_5)Cr]_{0.25}ZrS_2$, 62343-38-8; $[(\eta^8\text{-}C_8H_8)(\eta^5\text{-}C_5H_5)Ti]_{0.23}ZrS_2$, 67464-31-7.

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Low-Temperature Solution Preparation of Group 4B, 5B, and 6B Transition-Metal Dichalcogenides

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By use of nonhydroxylic solvents, the series of disulfides of the tetravalent transition metals of the left side of the periodic table are preparable via a simple metathetical reaction: $TX_4 + 2A_2S \rightarrow TS_2 + 4AX$. The crystallinity of the product TS_2 depends upon T and the conditions of the reaction, and particle sizes are in the submicron range. New amorphous phases have been found. The reactivity of these materials, in particular their intercalative behavior, is contrasted with those prepared by conventional high-temperature procedures. In certain cases, it is possible to obtain dispersions of TS_2, showing the effect of solvent.

Introduction

The transition-metal dichalcogenides of groups 4–6B are the focus of increasing attention as materials of interest in energy-related areas such as electrochemistry and catalysis.[1] In large part, their chemical and physical behavior derives from the fact that they crystallize in weakly interacting layers which allow for ready intercalation of appropriate species.[2] Conventionally, these compounds have been prepared only by high-temperature (above about 400 °C) methods such as direct contact of the elements in sealed tubes or vapor-phase reaction of the halides with hydrogen sulfide.[3] The elevated temperatures are necessary to attain reasonable rates of reaction and/or favorable thermodynamics. The products thus obtained are typically highly crystalline, are of low surface area, and are often nonstoichiometric and multiphased. These factors which occur in solid-state preparations can have pronounced effects on the chemical and physical properties of the materials, properties such as thermoelectric power, conductivity, rate of intercalation, etc.[4]

In this paper are described a series of novel means of preparing many group 4B, 5B, and 6B transition-metal layered dichalcogenides under moderate conditions by precipitation or slurry reactions in nonaqueous solutions much below 400 °C. The materials thus produced have physical properties and morphological characteristics radically different from those produced at higher temperatures. By appropriate adjustment of parameters, poorly crystalline or amorpous powders, gels, glasses, or homogeneous dispersions of the chalcogenides can

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be prepared. Additionally, normally crystalline compounds can be prepared, and because the preparations take place below 400 °C, portions of the transition metal–sulfur phase diagrams not previously studied are accessible. For example, we have recently reported the preparation of VS_2 by this method.[5] This compound was previously thought not to exist but recently its existence has been confirmed by preparation through oxidation of $LiVS_2$ in nonaqueous solvents.[6]

Low-temperature metathetical reactions in solution (eq 1)

$$TX_4 + 2A_2Y \xrightarrow{\text{soln}} TY_2\downarrow + 4AX \qquad (1)$$

T = group 4–6B transition-metal ion

X = salt anion (Cl^-, carboxylate, etc.)

A = alkali-like cation (Li^+, Na^+, NH_4^+, etc.)

Y = chalcogenide anion

present an attractive alternative means of preparation since they should be fast, simple, and allow for some control over parameters such as particle size and composition. Since both the transition-metal ions and chalcogenides are capable of existing in several oxidation states, redox reactions such as eq

$$TX_5 + {}^5/_2A_2Y \xrightarrow{\text{soln}} TY_2\downarrow + 5AX + {}^1/_2Y \qquad (2)$$

2 can also be conceived.

The high stability of the oxides and hydroxides of the early transition metals rules out aqueous environments for all such reactions; in fact, hydroxylic solvents in general (alcohols and carboxylic acids) are too reactive to serve as solvents for TX_4 or TX_5. Furthermore, hydrogen sulfide is not a viable source of chalcogenide ion at ambient temperature, since only traces of product form with $TiCl_4$, whether it is neat or is dissolved in a polar organic solvent.

We have found, and now report, that certain polar organic solvents are suitable media for the preparation of the dichalcogenides of the early transition metals, providing that appropriate sources of chalcogenides ion are employed. Of particular value in this respect are the lithium salts (Li_2S or LiHS) and the ammonium compounds.

Experimental Section

All of the manipulations were carried out in the rigorous absence of oxygen and water, since the products have been generally found to be very susceptible to oxidation. The transition-metal halides were obtained from various suppliers (Ventron, Atomergic, Pfalz and Bauer) and used as received, usually at least 99% pure. Similarly, the lithium sulfide (RIC/ROC or Ventron) and organic reagents were also not specially treated prior to their use. X-ray powder patterns were run on a standard Philips diffractometer with graphite-monochromated Cu Kα radiation. Optical microscopy was performed using a Leitz Orthlux-pol microscope and surface area measurements were ascertained using the Brunauer, Emmett, and Teller BET method based on nitrogen adsorption. TGA measurements were obtained with a du Pont thermoanalyzer.

As discussed below, reaction rates when Li_2S or Na_2S were used depended greatly upon the crystallinity of these materials. If the Li_2S or Na_2S was very crystalline, heating was required for precipitation reactions and the Li_2S or Na_2S would not react with neat $TiCl_4$. Poorly crystalline Li_2S or Na_2S reacts violently with pure $TiCl_4$. Commercial Li_2S and Na_2S have highly variable crystallinity and their reactivity cannot be predicted unless they are X-rayed to determine crystallinity. A convenient way of preparing highly reactive LiHS is to bubble excess H_2S through a solution of *n*-butyllithium in hexane which causes the white LiHS to precipitate from solution.

General Procedure. A solution of 0.01 mol of the transition-metal halide in about 30 mL of the organic solvent was made in a drybox under helium or nitrogen, and this was added to a well-stirred solution (or slurry) of 0.04 mol of poorly crystalline lithium sulfide in another 30 mL of the same solvent. After stirring of the mixture for several hours to 1 day, the dark precipitate formed was filtered in the drybox, washed with several portions of the solvent, dried, and weighed.

As an alternative to using lithium sulfide, ammonium or amine hydrosulfides were sometimes used. This was accomplished by first adding the transition-metal halide together with the amine or ammonia in the organic solvent and then bubbling in H_2S with a sparge for several minutes (until the reaction ceased). Precautions were taken to avoid allowing excess H_2S to escape into the atmosphere by attaching a NaOH bubbler to the reaction flask and working in a well-ventilated fume hood.

These reactions were all run at room temperature; however, in certain cases where rates were slow (such as when using crystalline Li_2S or Na_2S) heating was necessary. In some cases, the products were heat treated to enhance crystallinity and to drive off volatile coproducts or complexed solvent. Specific examples are given below in which the solvated products are usually obtained first, but the unsolvated product can always be obtained by pumping under vacuum with gentle heating.

Neat Preparation of Crystalline TiS_2 from NH_3, H_2S and $TiCl_4$. Into a three-necked flask, an excess quantity (approximately 5 g) of $(NH_4)HS$ or $(NH_4)_2S$ was prepared by flowing in NH_3 gas and H_2S gas. To the resulting white solid, 3.8 g of $TiCl_4$ (20 mmol) was added dropwise. A reaction immediately occurred yielding a black-brown solid, which was $TiS_2 + (NH_4)Cl$. This black-brown solid was removed from the flask and sealed under vacuum in a 20-mm diameter quartz tube which was 25 in. long. The tube was placed in a temperature gradient with one end at 380 °C and the other at 100 °C for 1 day. $(NH_4)Cl$ sublimed and condensed at the colder end thus effecting separation. At the hot end, the TiS_2 annealed yielding a highly crystalline X-ray powder pattern.

Preparation of Amorphous TiS_2 in Tetrahydrofuran (THF). A solution of 10 mmol of $TiCl_4$ (1.9 g) in tetrahydrofuran (75 mL) was made up in a drybox ($TiCl_4$ is not stable in air or moisture). To this stirred solution at room temperature was added 0.96 g (20 mmol) of poorly crystalline lithium sulfide. The yellow solution immediately began to darken. The reaction was allowed to proceed for several hours although it was essentially complete in 1 h. The resulting dark brown solid was filtered and washed with 10 mL of THF. The theoretical yield for TiS_2 was 1.12 g, but the product weighed 1.8 g or 38% too much. When heated to 200 °C in a TGA under inert atmosphere, the sample lost 39% of its weight, indicating the original black powder had the formula $TiS_2{\cdot}THF$. Throughout this work we found that the amorphous-layered sulfides would take up solvents which they would not normally intercalate. Chemical analysis of the initial black product powder showed that it was 63.6% TiS_2. Anal. Calcd: Ti, 27.18; S, 36.23. Found: Ti, 27.37; Si, 36.19. Small amounts of LiCl were also found because of incomplete washing. The $TiS_2{\cdot}THF$ product had a BET surface area of 14.2 m^2/g. If the product was treated with excess pyridine replacing the THF which was then driven out again by heating under vacuum, the surface area rose to 95.7 m^2/g and the product gave an amorphous TiS_2 X-ray pattern (Figure 5). The material was then annealed in a sealed quartz tube at 600 °C yielding a crystalline TiS_2 powder pattern with a 6.8 m^2/g BET surface area. (Precipitation directly in pyridine yielded gummy intractable products.)

Preparation of TiS_2 Dispersion and Gel. A 0.5-mL amount (0.86 g) of $TiCl_4$ was added to 20 mL of THF yielding a yellow solution. To this was added 5 mL of trihexylamine, which turned the solution brown. H_2S was bubbled through a solution which became thicker, opaque, and darker brown. No solid was seen and the liquid would not pass through a fine-fritted filter. After the mixture had stood overnight, a firm, glassy, black gel formed because of loss of THF.

Preparation of Amorphous ZrS_2, HfS_2, VS_2, and MoS_2. In an exactly analogous manner to the above preparations of TiS_2 and VS_2, ZrS_2, HfS_2, and MoS_2 were prepared from THF.

Preparation of Poorly Crystalline TiS_2 from Refluxing Acetonitrile. The following example employs as starting material $TiCl_4$. It was found that the procedure worked equally well for $ZrCl_4$, $HfCl_4$, or VCl_4. A 300-mL amount of 0.2 M $TiCl_4$ in acetonitrile was slowly added (1 drop/s) to a refluxing solution of 0.6 M Li_2S in acetonitrile. The solution was cooled, filtered, and washed with methanol to remove the LiCl formed. This was then followed by an ethyl ether wash, and the product dried on a Büchner funnel in a drybox. The resulting product was gold-brown and gave an X-ray pattern of TiS_2 with no further treatment.

Preparation of Amorphous NbS_2 (TaS_2). This procedure is applicable to those transition metals of group 5B which form pentahalides

(Nb and Ta), and the example is given for niobium pentachloride.

To a solution of 10 mmol of $NbCl_5$ (2.68 g) in 50 mL of tetrahydrofuran was added 1.15 g of poorly crystalline lithium sulfide (25 mmol), and the reaction was stirred in the drybox overnight. The dark product obtained on filtration was shown to contain 60% by weight $NbS_{1.97}$ corresponding to a composition of approximately $NbS_2 \cdot THF$. TaS_2 could be prepared in a similar manner but required a switch to ethyl acetate as a solvent.

Results

We may illustrate some general results by considering TiS_2. Even in the absence of oxygen from air to water, the reaction of $TiCl_4$ with H_2S has an unfavorable equilibrium direction at temperatures less than about 400 °C:

$$TiCl_4 + H_2S \overset{400\ °C}{\underset{\rightarrow}{\longleftarrow}} TiS_2 + 4HCl \qquad (3)$$

We have found that by using a more reactive (ionic) source for the chalcogenide (or equivalently by "activating" hydrogen sulfide by the addition of ammonia or amines) the reaction to form the transition-metal chalcogenides proceeds readily and quantitatively at ambient temperatures.

Lithium sulfide was found to be the most convenient source of sulfide ion:

$$TiCl_4 + 2Li_2S \xrightarrow{25\ °C} TiS_2 + 4LiCl \qquad (4)$$

Convenient solvents for ambient-temperature precipitation were tetrahydrofuran (THF) or ethyl acetate (EA). Both afforded dark precipitates which were easily filtered. The TiS_2 produced was amorphous to X-rays (Figure 5) but in other aspects such as reaction with *n*-butyllithium behaved as normal crystalline TiS_2. It proved difficult, however, to completely remove the LiCl because of the tenacious affinity of the highly active sulfide either on their surfaces or as inclusion compounds. However, repeated washings with the solvent would completely remove the LiCl.

Crystalline TiS_2 powders could be produced by heating amorphous TiS_2 at 400–600 °C in sealed quartz tubes with careful exclusion of oxygen. Poorly crystalline Na_2S or Li_2S reacts with $TiCl_4$ vigorously at room temperature. Crystalline TiS_2 could be produced by heating Na_2S with $TiCl_4$ in a sealed quartz tube. The LiCl formed is then washed out with 12% acetic acid. A very clean finely divided crystalline solid could be produced by heating the reaction product of NH_3, H_2S, and $TiCl_4$ to 400 °C in a sealed quartz tube. If one end was kept cool outside the hot zone, the NH_4Cl formed in the reaction would condense leaving the clean TiS_2 in the hot zone. The gold-green powder contained no significant chloride or oxide impurities.

Single crystals of TiS_2 up to 100 μ in diameter were grown from refluxing THF (tetrahydrofuran) in a Soxhlet extractor. Li_2S was placed in the extraction thimble and was slowly leached by refluxing THF. The flask contained 5.1 mL of $TiCl_4$ in 250 mL of THF. As Li_2S was carried into the flask by returning solvent, it reacted with the $TiCl_4$ to give TiS_2 and LiCl. This occurred quite slowly, and after about 2 weeks approximately 100 mg of golden crystals of TiS_2 was isolated from the flask. These crystals were well formed and ranged in size from 50 to 150 μ. This experiment clearly demonstrates that crystalline TiS_2 can be prepared from $TiCl_4$ and Li_2S at temperatures as low as 65 °C. It may be of interest in the future to compare the perfection of these crystals grown at 65 °C to that of crystals grown at higher temperature by solid-state methods, in particular the stoichiometry.

During the study of nonaqueous precipitation it was discovered that under various conditions gels could be produced. These gels, if pumped and heated to greater than 300 °C, yielded a black, glassy solid having an amorphous X-ray powder diffraction pattern. Scanning electron microscopy (SEM) revealed conchoidal fracture surfaces indicating that the product was a glassy phase, and X-ray fluorescence analysis showed titanium and sulfur. However, this glass was very air sensitive and when heated in air would spontaneously ignite and yield a new glassy substance which showed broad TiO_2 diffraction lines.

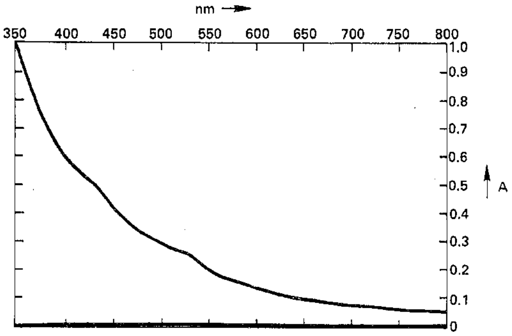

Figure 1. Absorbance vs. wavelength for 0.0025 M MoS_2 dispersion in propylene carbonate vs. propylene carbonate.

We may summarize the results as follows:

$$\begin{array}{l} TiCl_4 + 4NR_3 + 2H_2S \xrightarrow{THF} TiS_2 + 4R_3NHCl \qquad (5) \\ \quad R = hexyl \qquad\qquad\qquad\qquad gel \end{array}$$

The fact that the gel does not form when NH_3 is used instead of the long-chain amine suggests that the size of the R group is critical to gel formation. Probably the long-chain amines which would be complexed to the newly formed TiS_2 stabilized gel formation. The gel then decomposes as follows:

$$\begin{tikzcd} TiS_2\ gel \arrow[r, dash, "300\ °C", "{-THF \\ -HCl \\ -R_3N}"'] & TiS_2\ glass \arrow[r, "400\ °C"] \arrow[d, dash] & TiS_2\ crystalline \\ & {} \arrow[r, "400\ °C", "O_2"'] & TiO_2 \end{tikzcd} \qquad (6)$$

During the course of studying the room-temperature precipitation of the layered sulfides it became apparent that under a wide variety of conditions the precipitated solid remained completely or partially dispersed. For example, when a yellowish solution of $TiCl_4$ in PC (propylene carbonate) was added to a white slurry of Li_2S in PC, the solution immediately turned intensely black. No solids could be filtered out and this liquid remained stable for several years. Since we have established in several ways that the reaction of $TiCl_4$ with Li_2S is a straightforward one yielding TiS_2 + LiCl, we recognize that this black liquid was likely a colloidal dispersion of TiS_2 in the dense liquid PC. Although we are now in the process of fully characterizing these dispersions, evidence points to a colloidal dispersion of the sulfur–metal–sulfur layers. The higher surface area material produced as described above might be expected to disperse in the proper solvent. Indeed, Murphy[7a] and Lerf[7b] have reported the preparation of aqueous dispersions of TaS_2 produced by exfoliation and dispersion by blending with a surfactant. These dispersions were black with platelets in the 0.25–2-μ range but were unstable to hydrolysis by the aqueous solution. The dispersions made here often show a twinkling effect under high-power microscope objectives, but the particles giving rise to this effect are unresolved indicating that they are below 1 μ in size. The dispersions are optically very black, and no other detail above the general scattering background could be seen in visible-light transmission spectrographs which are shown in Figure 1.

Propylene carbonate was the most effective dispersing solvent tried with the concentration of TiS_2 reaching 0.2 M before solid began to separate. Other solvents were also able to disperse the layered sulfides to a greater or lesser extent. Generally, polar solvents with high viscosity and boiling points

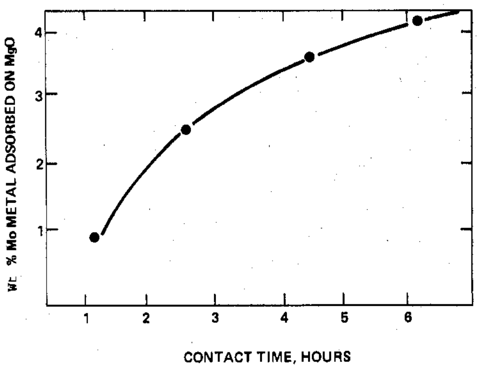

Figure 2. Percent Ti metal adsorbed on MgO for a constant contact time of 1 h vs. concentration of dispersion.

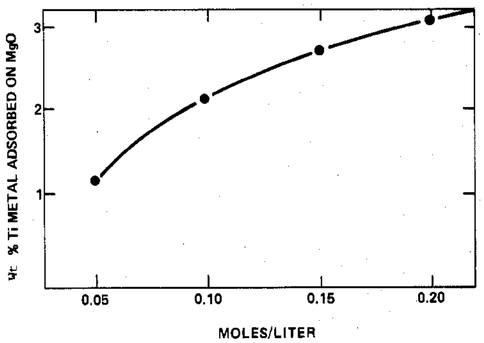

Figure 3. Percent Mo metal adsorbed on MgO from a 0.05 M MoS_2 in propylene carbonate dispersion as a function of contact time.

Table I. *n*-Butyllithium Uptake

sample	uptake, mol
TiS_2	1.09
VS_2	1.48
MoS_2	1.51

were the best dispersants. Dimethylformamide yielded wine-colored, purple, or dark blue dispersions depending upon the concentration which was generally lower than that obtained in propylene carbonate. Addition of amines such as pyridine increased the ability of a particular solvent to disperse.

The dispersed sulfides could be adsorbed from solution on basic oxides such as MgO or CaO because of the Lewis acid nature of the layered transition-metal sulfides or the nature of the polar adlayer. Adding sufficient basic oxide can entirely clear a solution. The amount of sulfide adsorbed (for a given stirring rate and particle size) depended upon the contact time with the dispersion and the concentration for a given basic oxide as indicated in Figures 2 and 3.

The amorphous sulfides reacted with a solution of *n*-butyllithium in hexane in a similar manner to that reported for the crystalline layered sulfides.[8] The amount of lithium taken for three samples is indicated in Table I. The amorphous TiS_2 was quite reactive. A sample of 100-mesh crystalline TiS_2 requires about 1 day to react completely with gaseous ammonia. Amorphous TiS_2, however, when contacted with ammonia vapor under ambient conditions in a gas buret adsorbed 1 mol within 5 min (no more was picked up).

We also wished to evaluate these materials as cathodes in lithium–nonaqueous batteries because of the recent advances in these systems using TiS_2 as a cathode material.[1] The amorphous TiS_2 was pressed on a nickel grid and placed in a cell with a lithium metal anode and a lithium perchlorate–ethereal electrolyte.[9] This cell had an open-circuit voltage of 2.55 V which is close to that of crystalline TiS_2. Amorphous VS_2 had an open-circuit voltage of 2.45 V and amorphous MoS_2 an open-circuit voltage of 2.23 V. A comparison of the cathodic properties of the amorphous dichalcogenides with those of their crystalline analogues will be the subject of a future report.

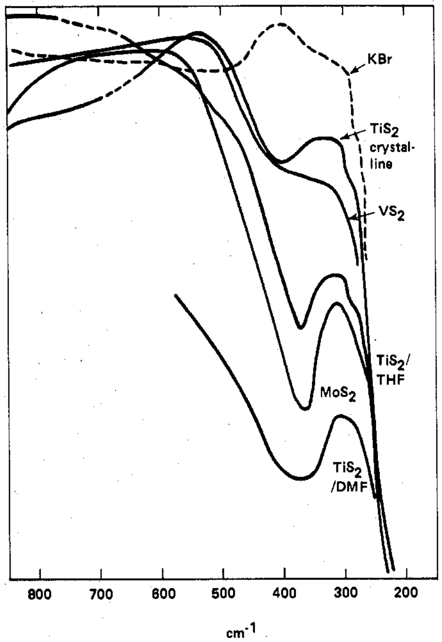

Figure 4. Far-infrared spectra of amorphous layered compounds.

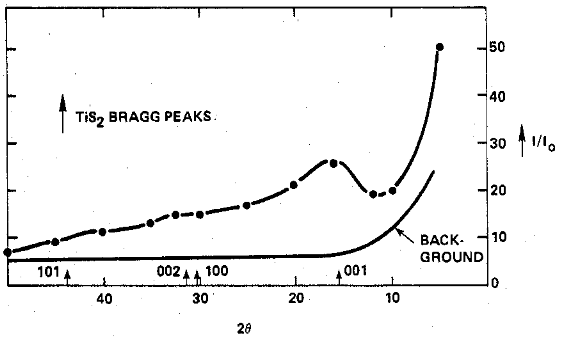

Figure 5. TiS_2 amorphous X-ray pattern.

Infrared spectra were obtained on a Beckman 12 spectrometer with the samples prepared in KBr disks. Sample preparation was in a drybox under nitrogen atmosphere. The results are indicated for several samples in Figure 4. The samples were quite susceptible to moisture in the amorphous state, particularly the group 4 sulfides. If any oxidation had occurred, it was immediately noticeable in the infrared by appearance of bands in the 900–1300-cm^{-1} region and by the disappearance or diminution of the M–S vibrations which appear in the 200–500-cm^{-1} region. IR spectra of pure samples show no other feature but the M–S vibrations. Crystalline and amorphous TiS_2 showed broad bands with the crystalline band appearing at 405 cm^{-1} and the amorphous band at about 365 cm^{-1}. The reason for this shift is not now understood. VS_2 showed a shoulder at approximately 400 cm^{-1}. The MoS_2 peak for poorly crystalline MoS_2 was broad and occurred at 365 cm^{-1} which is the same place at which the crystalline MoS_2 peak occurs. However, the width of this peak in MoS_2 is affected by crystallinity. Crystalline MoS_2 has a very narrow peak, poorly crystalline MoS_2, a very broad peak, and amorphous MoS_2, almost no infrared features at all. The infrared properties of these materials will be the subject of a future report.

X-ray diffraction patterns for the transition-metal sulfides ranged from completely amorphous, to poorly crystalline, to crystalline depending on preparation and treatment conditions.

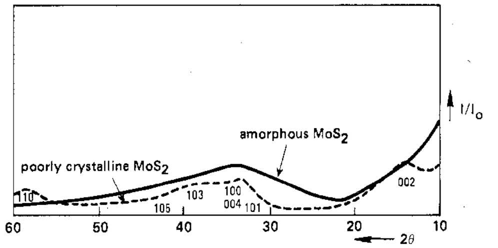

Figure 6. MoS_2 amorphous and poorly crystalline X-ray patterns.

In general there is an increasing tendency to stabilize lower crystallinity as one proceeds from group 4B to group 7B. Thus, MoS_2 is completely amorphous as prepared at room temperature and poorly crystalline when treated at 400 °C in H_2/H_2S. X-ray patterns are indicated schematically in Figures 5 and 6 for TiS_2 and MoS_2. The poorly crystalline X-ray pattern is very similar to that reported by Wildervanck and Jellinek[10] for MoS_2 prepared via decomposition of MoS_3 at 400 °C. However, the structure of amorphous MoS_2 below 400 °C has not been studied and is the subject of a future report.[11] TiS_2 and VS_2 tended to show slightly less amorphous X-ray patterns at room temperature. TiS_2 was completely crystalline when treated at 400 °C but again extreme care had to be taken to exclude oxygen due to the high stability of TiO_2.

Conclusion

By combining chalcogenide reagents more reactive (ionic) than H_2S (or by activating H_2S with ammonia or amines) with transition-metal salts in nonhydroxylic medium under ambient conditions, it is possible to prepare a broad-ranging series of transition-metal chalcogenides. Since most of these compounds have heretofore only been accessible via high-temperature procedures, in addition to offering a decided economical advantage due to rapid low-temperature procedures, this new route affords products showing distinctly different properties in many cases. These arise from surface area, crystallinity, particle size, phase, and stoichiometric characteristics resulting from the mild kinetic conditions of the preparation. Altogether new phenomena such as liquid and solid dispersions have also been observed, leading to many interesting avenues of future research for this group of materials. In addition, the structure and properties of the amorphous transition-metal disulfides will be the subject of intense investigation in the near future.

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Registry No. TiS_2, 12039-13-3; ZrS_2, 12039-15-5; HfS_2, 18855-94-2; VS_2, 12166-28-8; MoS_2, 1317-33-5; NbS_2, 12136-97-9; NH_3, 7664-41-7; H_2S, 7783-06-4; $TiCl_4$, 7550-45-0; Li_2S, 12136-58-2; $NbCl_5$, 10026-12-7.

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Intermolecular Energy Transfer between Lanthanide Complexes in Aqueous Solution. 1. Transfer from Terbium(III) to Europium(III) Complexes of Pyridinecarboxylic Acids

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Lanthanide complexes of picolinic, nicotinic, and dipicolinic acids have been studied using emission spectroscopy, lifetime of emission measurements, and pH titrations. In addition, energy transfer from Eu^{3+} to Tb^{3+} has been investigated. All of these measurements enable a description of the solution environment about the lanthanide ion when it is complexed to each of the pyridinecarboxylic acids. At high pH, the lanthanide complexes of dipicolinic acid are monomeric and discrete but probably are somewhat associated at low pH values. Complexes of picolinic acid are probably associated at all pH values. It was also concluded that picolinic acid can act as a bidentate ligand, that dipicolinic acid can act as a bidentate ligand at low pH and terdentate at high pH, and that nicotinic acid only functions as a monodentate ligand. The energy-transfer process was found to require the presence of mixed Tb^{3+}–Eu^{3+} complexes and polymeric formation.

Introduction

Various lanthanide ions are finding widespread use as spectroscopic probes of calcium binding sites in proteins and enzymes, since the calcium ion itself does not possess any useful spectroscopic properties. For instance, Tb(III) has been found to substitute for Ca(II) in a wide variety of proteins and the resulting sensitized emission enables the determination of important molecular properties.[1] In an effort to gain more information regarding the binding of lanthanides by proteins, many workers have undertaken studies of the complexation of lanthanide ions by carboxylic and amino acids in solution. These studies have included pH titrations,[2] difference absorption spectroscopy,[3] circular dichroism spectroscopy,[4] and circularly polarized emission spectroscopy.[5] The formation constants for lanthanide ions and a wide variety of carboxylic and amino acids have been reviewed,[6] as well as a number of solid-state crystal structures.[7]

It is well-known that energy may be transferred to and from lanthanide ions in solution.[8] Lanthanide ion emission is enhanced by organic molecules whose triplet levels lie just above those of the metal ion, and this emission enhancement seems to require some complexation of the lanthanide ion and the organic molecule.[9-11] Detailed studies have been made of the energy transfer between europium and terbium in dimethyl sulfoxide[12] and between europium and terbium β-diketonates in a variety of solvents.[13] Some energy-transfer studies involving lanthanide carboxylates have appeared,[5a,b] but these results have not received as full an interpretation as possible

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