and Cl$^-$, respectively. In both reactions $[Au(PPh_3)(AuPPh_3)_7]^{2+}$ is an intermediate and a possible mechanism is

$$[Au(AuPPh_3)_8]^{3+} \rightleftarrows [Au(AuPPh_3)_7]^{2+} + AuPPh_3^+$$

$$[Au(AuPPh_3)_7]^{2+} + PPh_3 \rightleftarrows [Au(PPh_3)(AuPPh_3)_7]^{2+}$$

$$[Au(PPh_3)(AuPPh_3)_7]^{2+} + X^- + 2e^- \rightarrow [Au_{11}] + \text{unidentified products}$$

To complete the number of electrons to 18, a reaction step leading to the Au_{11} cluster must be a reduction with 2 electrons. In fact, for the gold cluster compounds, disproportionation reactions are well-known.[21] The fragments can easily be oxidized. In platinum-gold cluster chemistry no such reactions are known and a phosphine addition to the central platinum completes the 18-electron configuration.

The complexity of the ^{31}P NMR spectrum may be due to a rigidity of the cluster compound $[Pt(PPh_3)(AuPPh_3)_6(AuX)_3]$. Normally, in solution at room temperature, the gold-phosphine sites in cluster compounds show a fluxional behavior, equilibrating all gold-phosphine sites so they yield a single peak in the ^{31}P NMR spectrum.[22,23] Another possible explanation for the complexity of the spectrum is the presence of different isomers. Because of the low solubility of the compound, it was not possible to use different NMR techniques (VT-NMR, 2D-COSY, ^{195}Pt) to establish the real cause for the complexity.

The $[Pt(CO)(AuPPh_3)_8]^{2+}$ and the $[Pt(H)(PPh_3)(AuPPh_3)_7]^{2+}$ clusters are 18-electron systems, and so the coordination of an additional nucleophilic ligand to the platinum center is not possible. It turned out that substitution is limited to the Au-bonded phosphines; the Pt-bonded PPh_3 and CO are inert to substitution.

The reactions of $[Pt(CO)(AuPPh_3)_8]^{2+}$ and $[Pt(H)(PPh_3)(AuPPh_3)_7]^{2+}$ with halides give $[Pt(CO)(AuPPh_3)_7(AuX)]^+$ and $[Pt(H)(PPh_3)(AuPPh_3)_6(AuX)]^+$, respectively, in high yields. Substitution is limited to a single PPh_3, even with a large excess of halide. This limit is also found in the substitution reactions with isocyanides.[2] An explanation could be the steric strain present in a system with eight PPh_3 groups and one CO. When one PPh_3 is replaced by a smaller ligand, the strain is removed and no further substitution will take place. The reaction of $[Pt(CO)(AuPPh_3)_8]^{2+}$ with two CN$^-$ ions in which $[Pt(CO)(AuPPh_3)_6(AuCN)_2]$ is formed is probably due to the high affinity of CN$^-$ for gold. Electronic properties of the incoming ligand will influence the chemical shifts and coupling constants of the ^{31}P NMR spectrum and the CO frequencies in the IR spectra (Table IV). A ligand with a higher electronegativity gives a lower electron density on the cluster, less shielding of the phosphorus atoms, and a slight increase of the chemical shift of the phosphorus atoms. Parallel goes a decrease of the $^2J(^{195}Pt-^{31}P)$ coupling constants, suggesting weaker Pt-Au-P bonding, and an increase of the CO frequency. For the $[Pt(H)(PPh_3)(AuPPh_3)_6(AuX)]^+$ clusters, the same trend is found for the $^2J(^{195}Pt-^{31}P)$ coupling constants (Table IV). However, the chemical shifts show an opposite trend. This phenomenon is also found for Ag, Au, Hg, and Pt complexes[24-28] and is summarized by Bos.[29] The reactions of $[Pt(CO)(Ag)(AuPPh_3)_8]^{3+}$ and $[Pt(H)(AuPPh_3)_8]^+$ with halides do not lead to simple substitution but to a decomposition of the starting clusters and complex reaction mixtures.

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Supplementary Material Available: Listings of complete crystallographic data and data collection parameters, additional temperature factors, fractional positional parameters, thermal parameters, and bond distances and angles (14 pages); a listing of observed and calculated structure factors (56 pages). Ordering information is given on any current masthead page.

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Contribution from the Chemistry Department, Polytechnic University,
333 Jay Street, Brooklyn, New York 11201

Low-Temperature Synthesis of Vanadium Sulfides

A. Bensalem* and D. M. Schleich

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The ambient-temperature reactions between VCl_4 and the sulfurizing agents $[(CH_3)_3Si]_2S$, $[(CH_3)_3C]_2S_2$, $[(CH_3)_3C]_2S$, and H_2S have been studied. We have observed that VCl_4 reacts differently from other transition-metal halides when sulfurized at low temperature. Indeed, the low-temperature sulfurization of VCl_4 almost always yields amorphous VS_4, with the formation of S-S bonds. The only exception we have observed is the reaction of VCl_4 with Li_2S, which yields Li_xVS_2.

Introduction

Layered transition-metal disulfides are of great interest due to their electronic properties, catalytic behavior, and insertability.[1,2] Conventionally, most of the transition-metal disulfides are prepared by stoichiometric reactions of the elements above 500 °C.[3-5]

In the group 4 and 5 transition-metal sulfides MS_2, VS_2 is the only compound that has not been prepared by direct combination of the elements. In the vanadium-sulfur system, V_5S_8 appears to be the most sulfur-rich vanadium sulfide that can be prepared by reaction between the elements.[6,7] Chianelli and Dines[8] at-

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tempted to produce vanadium disulfide at room temperature by reacting VCl_4 (dissolved in a polar solvent) with the ionic sulfide Li_2S. The amorphous vanadium sulfide prepared in this way is coprecipitated with ionic halides, which must be removed to obtain a pure product. In addition, the infrared spectra of the purified amorphous powder showed a large anomalous absorption in the 400–500 cm^{-1} region.

On the other hand, Murphy and co-workers[9] have been able to prepare polycrystalline VS_2 with the CdI_2 structure by removing lithium from $LiVS_2$ through reaction with iodine in an acetonitrile solution. This was the first report of the preparation of VS_2.

Hexamethyldisilthiane (HMDST) has been effectively used as a low-temperature agent in the sulfurization of metal halides.[10–17] The reports on HMDST indicated that the reaction using this sulfurizing agent is based on an exchange of two halogens for one sulfur:

$$MCl_n + (n/2)[(CH_3)_3Si]_2S \rightarrow MS_{n/2} + n(CH_3)_3SiCl \qquad (1)$$

Theoretically, 2 mol of HMDST is needed to react with 1 mol of VCl_4 in order to prepare VS_2. In the present work, an attempt was made to prepare amorphous VS_2 through the low-temperature reaction of VCl_4 with the following different sulfurizing agents: hexamethyldisilthiane (bis(trimethylsilyl) sulfide), $(CH_3)_3SiSSi(CH_3)_3$; di-*tert*-butyl disulfide (2,2-dithiobis(2-methylpropane)), $(CH_3)_3CSSC(CH_3)_3$; di-*tert*-butyl sulfide (2,2-thiobis(2-methylpropane)), $(CH_3)_3CSC(CH_3)_3$; lithium sulfide, Li_2S; and H_2S.

Experimental Section

(A) Synthesis. All the reactions were performed under an inert atmosphere, since the products have been generally found to be very reactive to both moisture and air. The organic sulfurizing agents were obtained from Fluka Chemical Corp. and were fractionally redistilled immediately before the reactions under dry argon after refluxing with calcium hydride to remove water. For each reagent, the material used for the reaction was collected over a 2-deg range of its boiling point. The collected reagents were transferred into the reactor under argon. Vanadium tetrachloride was obtained from Alfa Products and was dissolved in dry methylene chloride and kept under a dry argon atmosphere. Due to the extreme reactivity of VCl_4 with moisture, care had to be taken in introducing it to the organic sulfurizing agent. This was accomplished by using a stainless steel transfer tube under argon.

Reaction of VCl_4 with HMDST. The hexamethyldisilthiane used for the reaction was collected over a 2-deg range of its boiling point (160–162 °C) during the fractional distillation. A 15-mL sample of VCl_4 dissolved in 50 mL of CH_2Cl_2 was used to react with 80 mL of HMDST corresponding to 2.6 mol of HMDST for 1 mol of VCl_4. The reaction occurred spontaneously and exothermically at room temperature. The reaction mixture was stirred at room temperature for 12 h. The resulting precipitate was filtered out under dry nitrogen and washed with dichloromethane, after which it was washed with dried tetrahydrofuran (THF) in a Soxhlet extractor to ensure complete removal of any unreacted halides.

Reaction of VCl_4 with Di-*tert*-butyl Disulfide. A 15-mL sample of VCl_4 dissolved in 50 mL of dichloromethane was added to 30 mL of distilled di-*tert*-butyl disulfide (DTBDS) (bp 200–202 °C) corresponding to 1.1 mol of DTBDS for 1 mol of VCl_4. The reaction was very slow, and the temperature was then increased to refluxing conditions for 12 h. Filtration and washing were performed as above.

Reaction of VCl_4 with Di-*tert*-butyl Sulfide. A 15-mL quantity of VCl_4 dissolved in 50 mL of dichloromethane was added to 50 mL of distilled di-*tert*-butyl sulfide (DTBS) (bp 148–150 °C) corresponding to 2 mol of DTBS for 1 mol of VCl_4. The reaction mixture was heated to reflux for 12 h. Filtration and washing were carried out as indicated above.

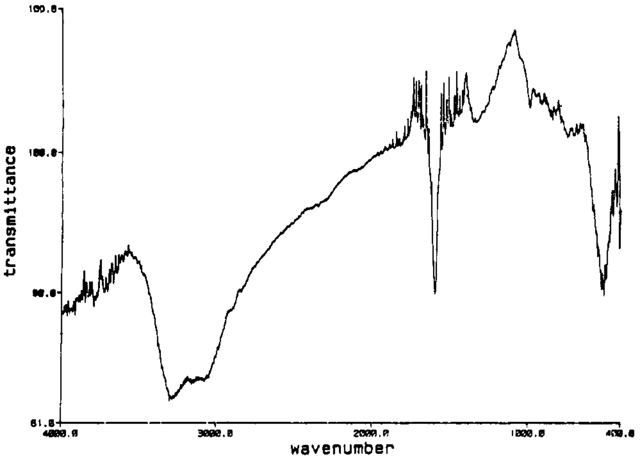

Figure 1. FTIR spectrum of the obtained powder before washing with THF.

Reaction of VCl_4 with H_2S. The reaction was performed at room temperature by passing H_2S gas into 10 mL of VCl_4 diluted with 30 mL of dichloromethane. A reaction occurred spontaneously, and a brown precipitate was formed. Filtration and washing were performed as above.

Reaction of VCl_4 with Li_2S. The reaction between 1.60 mL of VCl_4 diluted in 10 mL of THF and 1.40 g of Li_2S diluted in 30 mL of THF (corresponding to 2 mol of Li_2S for 1 mol of VCl_4) was performed at room temperature. The reaction occurred spontaneously and exothermically and led to a formation of a black precipitate. After the reaction mixture was stirred for 10 h, the filtration and washing processes were performed as above.

Delithiation Reaction. A 0.3-g sample of the powder obtained from the reaction between Li_2S and VCl_4 was reacted with 6.7 mL of 0.2 N iodine solution in dry THF. The reaction mixture was stirred for 20 h under argon atmosphere. Filtration and washing were as above.

(B) Characterization. The liquids collected after filtration were analyzed by proton NMR spectroscopy using a Varian EM-390 90-MHz NMR spectrometer. The purified powders were analyzed by X-ray diffraction using a Phillips XRD 3100 diffractometer. Thermogravimetric analyses (TGA) were performed with a Stanton Redcroft TG 760 thermobalance, Model 761. Infrared studies were performed by using a Digilab Division FTS-60 FTIR spectrometer with an instrumental resolution of 4.00 cm^{-1}. The FTIR spectra were taken on KBr pellets. The spectra were composites of 64 individual scans and were all taken under a dry nitrogen atmosphere at room temperature. Chemical analyses of the purified powders were performed by Galbraith Laboratories, Inc.

Results and Discussion

Theoretically, 2 mol of HMDST is needed to react with 1 mol of VCl_4 in order to prepare VS_2. An excess of HMDST (molar ratio 2.6/1) was used in order to ensure completion of the reaction. The obtained degassed powder was analyzed by X-ray powder diffraction, and the results showed the existence of a crystalline phase identified as $VCl_3 \cdot H_2O$ superimposed on a part of the spectrum that is amorphous to X-rays. In order to confirm these observations, an infrared study was performed on this powder. The infrared spectrum of this powder in the region 400–4000 cm^{-1} is shown in Figure 1. This spectrum presents strong similarities with the spectrum of $VCl_3 \cdot H_2O$. A broad peak is also observed at 575 cm^{-1}, which could be assigned to a S–S stretch[18] in the amorphous component of the sample. The formation of $VCl_3 \cdot H_2O$ must be due to some unreacted VCl_4 remaining in the obtained sample after filtration, although the reaction has been performed in excess HMDST. The sample was then purified in a Soxhlet extractor by washing with dry tetrahydrofuran. The purified powder was amorphous to X-rays, showing no Bragg reflections. However, the FTIR spectrum of this purified powder (Figure 2) still shows the existence of an absorption at 540 cm^{-1} assigned

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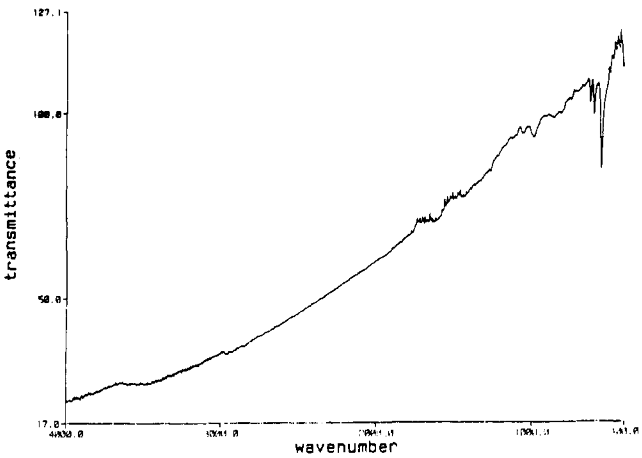

Figure 2. FTIR spectrum of the purified powder after washing with THF by using a Soxhlet extractor.

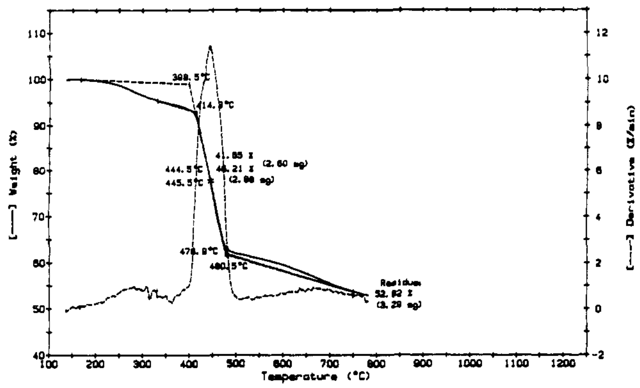

Figure 3. TGA (under nitrogen) of the purified powder.

to a S–S stretch, which indicates that the obtained amorphous powder is a sulfide phase with S–S pairs and not VS_2. Indeed, Chemical analysis of the purified powder shows a sulfur to metal ratio of 1/3.94.

Thermogravimetric analyses (TGA) under air and under nitrogen were performed to analytically characterize the sample. Using TGA in air, we calculated the composition of the amorphous powder from the weight change of the sample after oxidation in air to V_2O_5 at 600 °C, assuming that only vanadium and sulfur were present in the amorphous powder. The composition of the amorphous powder was determined to be $VS_{4.2}$. The thermal stability of the amorphous powder was studied by using TGA under nitrogen (Figure 3). This result shows that our amorphous powder is stable up to approximately 400 °C. At 400 °C, it starts to lose sulfur and transforms to V_5S_8 at about 500 °C. According to Jellinek,[6] VS_4 decomposes with sulfur loss at approximately 400 °C.

Another confirmation of the formation of VS_4 is given by the results of the NMR studies of the collected filtrate. Indeed, the NMR spectrum shows the formation of only about 2 mol of trimethylchlorosilane/mol of VCl_4 (instead of the expected 4 mol of trimethylchlorosilane/mol of VCl_4 as shown by reaction 1) and reveals the formation of hexamethyldisilane, $(CH_3)_3SiSi(CH_3)_3$, and the absence of HMDST although an excess of 0.6 mol of HMDST/mol of VCl_4 was used. A possible reaction explaining the products obtained could be as follows:

$$VCl_4 + \tfrac{8}{3}[(CH_3)_3Si]_2S \rightarrow \tfrac{2}{3}VS_4 + \tfrac{1}{3}VCl_4 + \tfrac{8}{3}(CH_3)_3SiCl + \tfrac{4}{3}(CH_3)_3SiSi(CH_3)_3 \quad (2)$$

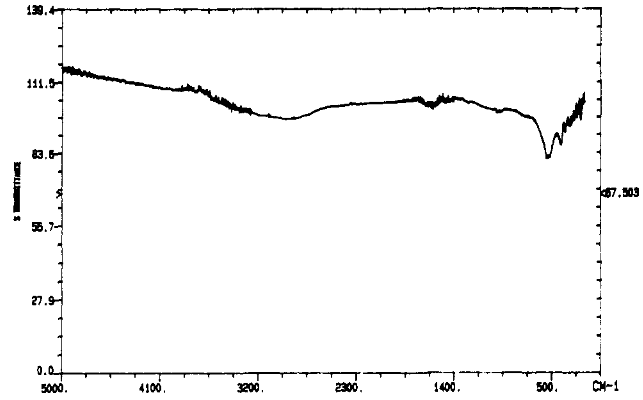

Figure 4. FTIR spectrum of the amorphous powder obtained from the reaction using 4 mol of HMDST/mol of VCl_4.

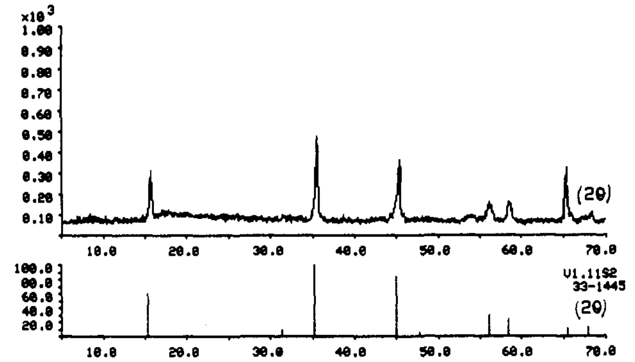

Figure 5. X-ray diffraction patterns of the sample heated at 400 °C under dynamic vacuum for 10 h.

The reaction does not seem to be a metathesis reaction, it is actually a redox process involving in part the oxidation of S^{2-} to S_2^{2-} and leading then to the formation of VS_4 instead of VS_2. The formation of $VCl_3{\cdot}H_2O$ is due to the existence of unreacted VCl_4. Indeed, as shown by reaction 2, 4 mol of HMDST is needed to complete the reaction of 1 mol of VCl_4 if VS_4 is formed. With the use of only 2.6 mol of HMDST/mol of VCl_4, one-third of the vanadium tetrachloride remains unreacted. VCl_4, being highly reactive with air and moisture, is readily converted to $VCl_3{\cdot}H_2O$. In order to confirm this, we reacted 4 mol of HMDST/mol of VCl_4 (with 10% excess of HMDST). The NMR spectrum of the collected filtrate shows the formation of 4 mol of trimethylchlorosilane and 2 mol of hexamethyldisilane/mol of VCl_4. The formation of 4 mol of $(CH_3)_3SiCl$/mol of VCl_4 confirms the complete reaction of VCl_4. The complete reaction of VCl_4 is also well shown by the FTIR spectrum of the obtained powder (Figure 4). Indeed the infrared spectrum of this powder shows the existence of the absorption assigned to S–S pairs (related to the formation of VS_4) and no sign of any V–Cl stretching vibrations. The total reaction between VCl_4 and HMDST can be written as

$$VCl_4 + 4[(CH_3)_3Si]_2S \rightarrow VS_4 + 4(CH_3)_3SiCl + 2(CH_3)_3SiSi(CH_3)_3$$

It appears from these analyses that the reaction between VCl_4 and HMDST leads to the formation of VS_4. We tried to prepare VS_2 by thermal degradation of our amorphous VS_4. The amorphous powder was heated at 350 °C under dynamic vacuum (10^2 Pa) for 10 h. The powder remaining in the hot part of the tuve was amorphous to X-rays, and the FTIR spectrum of this powder still showed the S–S vibration. However, the V/S ratio determined by thermogravimetric analysis was found to be 1/3. The amorphous VS_4 was then heated at 400 °C in an evacuated sealed tube for 10 h. A sulfur deposit was observed in the cold end of the tube. The powder remaining in the hot part of the tube crystallized in several vanadium sulfide phases, among them VS_4. The amorphous VS_4 did not seem to rapidly decompose at 400 °C in an evacuated sealed tube. However, when this powder was heated at 400 °C under a dynamic vacuum for 10 h, it transformed to a crystalline phase of the type $V_{1+x}S_2$ (Figure 5). The V/S ratio was determined by thermogravimetric analysis to be 1/1.85. The conversion of amorphous VS_4 into a crystalline $V_{1+x}S_2$ phase was observed in the infrared spectrum by the disappearance of the S–S vibration. When amorphous VS_4 was heated in an

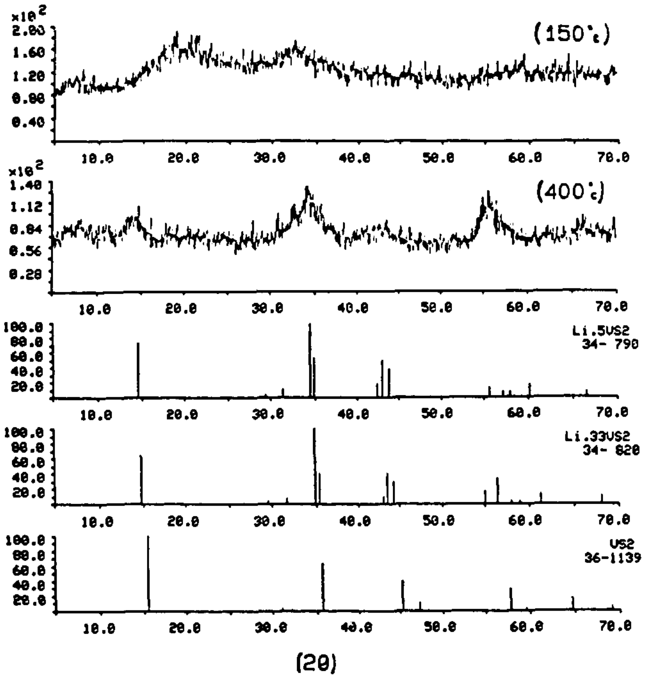

Figure 6. X-ray diffraction patterns of the powder obtained from the reaction between Li_2S and VCl_4.

evacuated sealed tube at 550 °C for 10 h, the powder crystallized as V_5S_8.

The reaction of 1 mol of VCl_4 with 2 mol of HMDST, even if it occurs without reduction or oxidation of the starting vanadium (V^{4+}), does not lead to the formation of VS_2. The study of the low-temperature sulfurization of VCl_4 was completed by reacting VCl_4 with DTBDS, DTBS, H_2S, and Li_2S.

The reaction of VCl_4 with either DTBDS or DTBS was very slow, and the reaction temperature had to be increased (refluxing conditions). Although these reactions yield the expected byproduct (*tert*-butyl chloride, $(CH_3)_3CCl$), the reaction mechanisms are not clear. Indeed, the NMR analysis of the collected filtrate show the existence of several other organic byproducts. After the purification process, the obtained powder was analyzed by X-ray diffraction. The results indicated the formation of poorly crystalline VS_4. The same result was observed for the reaction with H_2S. Indeed, the spontaneously formed brown prtecipitate was identified to be a poorly crystalline VS_4 by X-ray diffraction. Following the work of Chianelli and co-workers,[8] we performed a reaction between VCl_4 and Li_2S. X-ray diffraction of the purified powder (Figure 6) shows that the amorphous powder crystallizes (when heated to 450 °C) in a phase with an X-ray diffraction pattern closer to that of Li_xVS_2 than that of VS_2. Indeed chemical analysis of the amorphous powder indicates the existence of approximately 2/1 Li/VS_2. The formation of a lithiated VS_2 is noticeable in the infrared spectrum by the appearance of Li–S vibrations[19] in the 400–500-cm^{-1} region (Figure 7). Following the work of Murphy and co-workers,[9] in which they reported a possible delithiation of $LiVS_2$, we reacted the amorphous powder (obtained from the reaction with Li_2S) with an iodine solution. The oxidation of the sample by the iodine solution is shown in the infrared spectrum by the disappearance or the diminution of the Li–S vibrations (Figure 8). This last observation confirms that the room-temperature reaction of VCl_4 with Li_2S does not yield VS_2; the obtained phase appears to be a lithium–vanadium–sulfur phase with a VS_2 structure that is probably stabilized by the existence of lithium.

Conclusion

In this work, we have demonstrated that the low-temperature sulfurization of VCl_4 produces the VS_4 phase. We also noticed

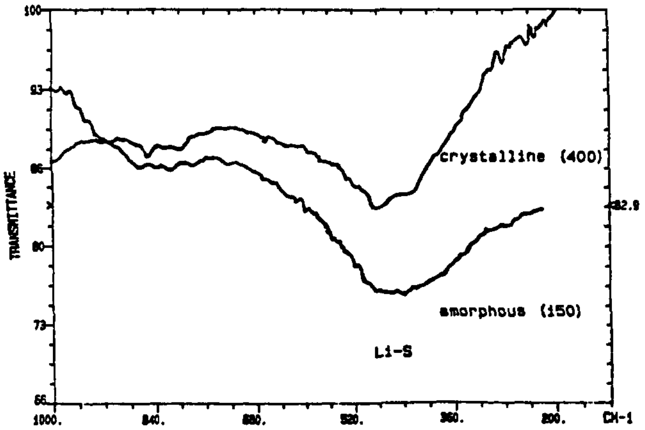

Figure 7. FTIR spectrum of the unheated amorphous powder along with the spectrum of the same powder heated at 400 °C (reaction of VCl_4 with Li_2S).

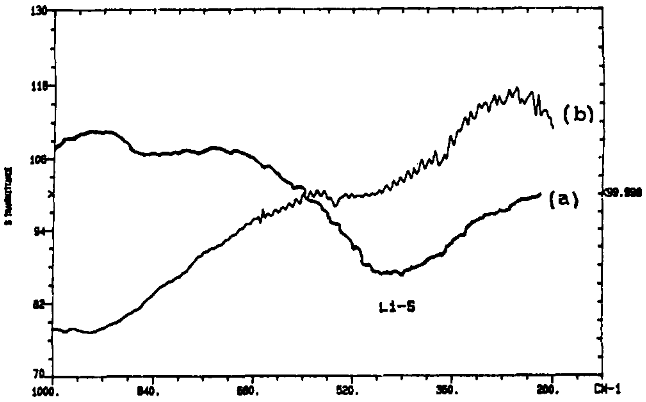

Figure 8. FTIR spectra of the amorphous powder obtained from the reaction of VCl_4 with Li_2S: (a) before oxidation with the iodine solution; (b) after oxiatino with the iodine solution.

for the first time that a reaction using HMDST and a metal halide has resulted in the formation of a sulfur compound that cannot be explained by the simple exchange of two chlorines for one sulfur and that the reaction is more complicated than can be explained by a simple metathesis type reaction.

The highest crystalline vanadium sulfide that can be formed from the thermal decomposition of amorphous VS_4 is $VS_{1.85}$. However, we believe that amorphous VS_2 could be obtained by varying the temperature and the sulfur vapor pressure inside the tube containing VS_4. We observed that amorphous materials with a S/V ratio of 3/1 could be obtained.

VS_4 appears to be the most stable phase at low temperature in the vanadium/sulfur system; however, this observation seems to vary with the results of Chianelli and Dines.[8] Thus we have performed the same reaction ($2Li_2S + VCl_4$) at room temperature, and it appears that the obtained amorphous powder is Li_xVS_2 rather than VS_2. Vanadium disulfide could be prepared from this compound by removing the lithium from the obtained Li_xVS_2.[9]

This behavior of vanadium is totally different from those we have observed for Nb, Mo, Cr, W, and Fe, where the reaction is well-described by eq 1. It appears that this transition metal, when found in a formal 4+ oxidation state, induces the formation of S–S bonds even at room temperature. The addition of a very electropositive element such as Li hinders the formation of the disulfide bonds and allows for the formation of a lithiated VS_2 with a CdI_2 type layered structure.

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