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Reaction of *n*-Butyllithium with Transition Metal Trichalcogenides[1]

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Optical, ir, chemical, and X-ray diffraction data show that the reaction of *n*-butyllithium with the trichalcogenides MX_3 yields compounds of type Li_3MX_3. The reactions proceed topochemically with MX_3 chains remaining intact after Li uptake. X-Ray powder diffraction patterns can be indexed on an expanded monoclinic lattice (Li_3TiS_3: a = 11.1 Å, b = 3.46 Å, c = 9.12 Å, and β = 98.0°) with b axis (chain axis) remaining constant. Ir (Li_3TiS_3) shows disappearance of polysulfide vibration (560 cm^{-1}) and appearance of only two vibrations (425 cm^{-1} Li–S and 220 cm^{-1} Ti–S) indicating higher symmetry.

Introduction

Recently, Dines has described the reaction of *n*-butyllithium with the layered transition metal dichalcogenides and trichalocogenides to yield lithiated products.[2] We have discovered that the reaction of *n*-butyllithium and other lithiating agents with the transition metal trichalcogenides proceeds topochemically to yield ternary phases of the type Li_3MX_3.

$$3CH_3(CH_2)_3\text{–}Li + MX_3 \rightarrow Li_3MX_3 + {}^3/_2CH_3(CH_2)_6CH_3 \quad (1)$$
$$M = Ti, Zr, Hf, Nb; X = S, Se$$

The transition metal trichalcogenides have structures[3,4] with chains of distorted trigonal prisms of MX_6 infinitely extending parallel to the b axis of monoclinic cells. These chains occur in pairs with each member translated 0.5 unit cell. Chain pairs are separated by van der Waals gaps of polysulfide ions as seen in Figure 1. The transition metal trichalcogenides which may be viewed as $M^{4+}(S_2^{2-})(S^{2-})$ retain the chain structure upon uptake of Li during reaction with *n*-butyllithium. It is the purpose of this report to describe this reaction and the structure and properties of the product.

Experimental Section

The trichalcogenides were prepared by direct combination of the elements or by sulfur vapor transport as outlined by Haraldsen et al.[5] All reactions were carried out in sealed quartz tubes. Reagents were supplied by Ventron Corp., Beverly, Mass. or by Research Organic/Inorganic Corp., Bellville, N.J. Where large single crystals were desired, the reaction tube was placed in a temperature gradient of about 50° (typically for TiS_3 this was 550–500°). Excess sulfur would transport crystals to the cold end. Crystals up to 1 cm × 0.2 cm × 0.1 mm can be obtained by this method.

All lithiations were done in a dry N_2 or He atmosphere. The *n*-butyllithium was obtained from Foote Mineral Co., Exton, Pa., as a 1.6 *M* solution in hexane. Typically, the reagent was diluted with hexane prior to use and a solution which was 50% excess in *n*-butyllithium (50% in excess of 3 mol of lithium per mole of trichalcogenide) was added to a known amount of the solid trichalcogenide. After several days of standing at room temperature, the solid was filtered, washed with pentane, and dried. The combined filtrates were assayed for active remaining *n*-butyllithium by adding a known excess of 0.1 *N* HCl. This was then titrated with standard base to an end point determined by a phenolphthalein indicator. The reaction as shown in eq 1 also produces octane and this was determined by gas chromatography in some cases. A full discussion of this technique has been given by Dines.[2] In several cases, stoichiometric or less than stoichiometric amounts of *n*-butyllithium were added. As a typical example we give the following.

Preparation of Li_3TiS_3. After allowing 0.182 g of TiS_3 (1.26 mmol) to react with 6.18 mmol of *n*-butyllithium in 12 ml of hexane for 3 days the solid was filtered, washed once with hexane, and dried. Using the back titration technique the combined filtrates were found to contain 2.37 mequiv of active reagents (and 1.25 mmol of octane, or 66% theoretical). This corresponds to an uptake of 3.02 mmol of Li per TiS_3 unit. The dilution and time allowed did not affect the stoichiometry of uptake in this case. The resulting products were free-flowing powders.

The reactions of single crystals of trichalcogenides with *n*-butyllithium were followed optically by placing the reactants in a sealed Beckman optical cell (1 mm path length) and viewing the contents of the cell under a Leitz Ortholux II optical microscope equipped with reflected and transmitted polarized light.

X-Ray powder diffractograms were taken with a Philips diffractometer and Ni-filtered Cu Kα radiation. All samples were prepared in Mylar covered sample holders under inert atmosphere.[6] The resulting powder patterns were of poor quality with broad diffuse lines indicating poorly crystalline materials. In most cases long exposure (12 hr) Debye–Scherrer photographs yielded significantly better results. Infrared spectra were obtained with a Beckman 12 spectrophotometer using Marcol mulls prepared in dry atmosphere.

Results and Conclusions

Reaction with *n*-Butyllithium. The reaction of *n*-butyllithium with the trichalcogenides proceeds without bubbling or gas evolution, but with some generation of heat. In each case, a distinct color change was noted and a summary of the results of lithiation is included in Table I. In general, the trichalcogenides appeared to obtain the stoichiometry Li_3MX_3. The Hf trichalcogenides appeared to require longer times for complete uptake and the compounds, ZrS_3 and $ZrSe_3$, tended to take up more than three lithium atoms; however, the X-ray and infrared evidence described below showed the same crystalline phases in all cases. When given just 3 equiv, ZrS_3 and $ZrSe_3$ took up all and gave more crystalline X-ray patterns than when excess was given. Li_3ZrS_3 and Li_3ZrSe_3 are the most reactive of the Li trichalcogenides. They react pyrophorically in air and the slightest trace of water or air will cause the green powder to return instantly to the original orange form. The Hf analogs are more stable and appear to reach the end point of three Li without consuming more. Li_3TiS_3 is the most stable of the group 4B trichalcogenides prepared. Some were prepared by two other methods, the lithium naphthalide method[7] or Li dissolved in liquid NH_3, both of which gave essentially the same results as *n*-butyllithium. A solution of lithium naphthalide was prepared which contained just 3 equiv of Li per equivalent of trichalcogenide. The dark lithium naphthalide solution cleared indicating that all three lithiums had been taken up by the $ZrSe_3$. In general, the products gave better powder patterns if they were initially given only a stoichiometric amount of lithium. In the case of TiS_3, 1 equiv of lithium yielded Li_3TiS_3 and TiS_3 as determined from X-ray and infrared evidence which indicates that nonstoichiometric compounds are not formed. However, in cases (Zr, Hf) when more or less than 3Li are taken up nonstoichiometric compounds are indicated. A kinetic run was performed in which aliquots were taken from a reaction mixture with time and analyzed for remaining Li with *n*-butyllithium and TiS_3 as shown in Figure 2. It can be seen that the first two lithium atoms are taken up within 1 hr and that three are taken up in 6 hr. In two cases (Ti or Hf) lithium uptake and octane yields were confirmed by chemical analysis. Concentration and dilution of the *n*-butyllithium had little effect on the uptake of Li. In summary the trichalcogenides either attained the stoichiometry Li_3MX_3 (TiS_3, $HfSe_3$, $NbSe_3$) or could be prepared with this stoichiometry by either reacting with only

Table I. Summary of *n*-Butyllithium Reactions with Transition Metal Trichalcogenides[a]

MX_3	Li added, (equiv)	Lithium uptake, (equiv)	Time allowed, days	Remarks	Color change
TiS_3	1	1	4	Two phases (66% octane)	Silvery black to flat black
	4.9	3.02	4		
	5.7	3.05[b]	4		
ZrS_3	1.5	1.5	6	73% Octane	Orange to dark green
	3[d]	2.8	1		
	4.5	4.5	6		
	10	5.5	4		
	3[d]	3	1	$Li-NH_3$ used 1.6 equiv after 7 hr	
$ZrSe_3$	6	5	5		Brown to black
	4.6	2.90	5		
HfS_3	8	2.5	3		Orange to green
	3	2.2[c]	5		
	4.6	2.7	5		
$HfSe_3$	6	2.9	4	1.5 equiv after 7 hr	Brown to black
	3[d]	3	4	Li naphthalide used	
NbS_3	3	2.2	5	88% octane	Lustrous to flat black
	5	2.24	6		
$NbSe_3$	5.9	3.4	6	74% octane	Same as NbS_3
	5.1	3.16	7		

[a] Chemical analyses were performed by Swarzkopf Analytical Laboratories. [b] Observed stoichiometry $Li_{3.07}TiS_3$. [c] Observed stoichiometry $Li_{2.2}HfS_3$. [d] Prepared by means of lithium naphthalide or lithium–ammonia.

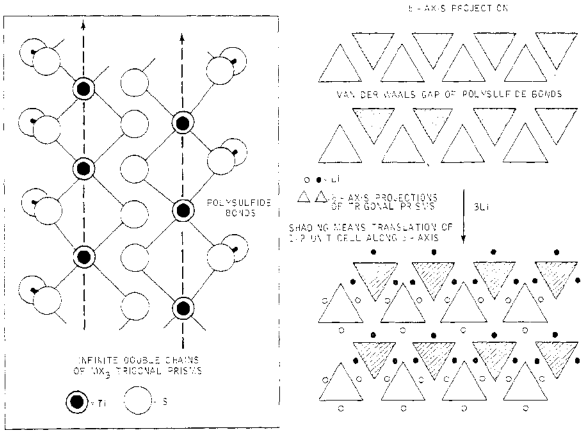


Figure 1. Schematic representation of the structure of MX_3 and proposed structure of the lithiated product Li_3MX_3.

three Li (ZrS3, ZrSe3) or by reacting excess for longer periods (HfS3, NbS3).

Optical Microscopy. The trichalcogenides have either a needle-like or board-like (pinacoidal) morphology with the *b* axis of the monoclinic cell along the needle axis. TiS3 and the group 5B crystals are silvery-black reflective crystals, but when viewed in transmitted light, thin crystals are partially transparent with a red to orange color. Hafnium and zirconium trisulfide crystals are red-orange and are transparent in transmitted light. The corresponding triselenides are less transparent and are silvery-black in bulk. All crystals extinguished cleanly in reflected or transmitted polarized light along their needle axes. When reacted with *n*-butyllithium, TiS3 appears to become fluffier in the bulk and microscopic examination after lithiation shows that the smaller individual crystals have retained their crystalline integrity as seen from the fact that they extinguish cleanly as before. Trichalcogenide single crystals were placed in Fisher quartz spectrophotometer cells and the *n*-butyllithium was added to the cell with a syringe in a dry atmosphere. The reaction was then followed under the microscope with time. In several cases the same crystal was observed throughout the reaction. When placed in *n*-butyllithium a TiS3 crystal almost immediately began to lose reflectivity and became black. At the same time striations appeared along the *b* axis. This process continued and small crystals began to separate from the edges as shown in Figure 3. When complete the larger crystals were heavily striated but still extinguished polarized light along the *b* axis. Many perfect small single crystals had separated from larger crystals. The same behavior was observed with HfS3 in transmitted light

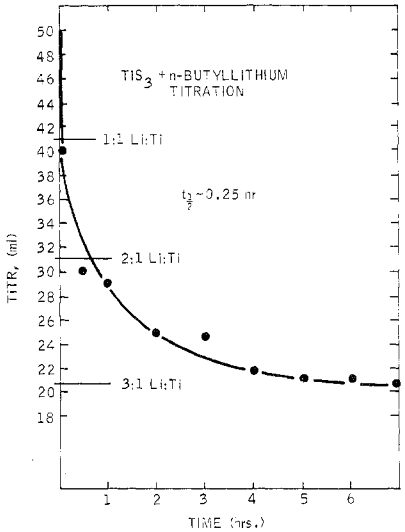


Figure 2. Kinetic uptake of Li by TiS_3.

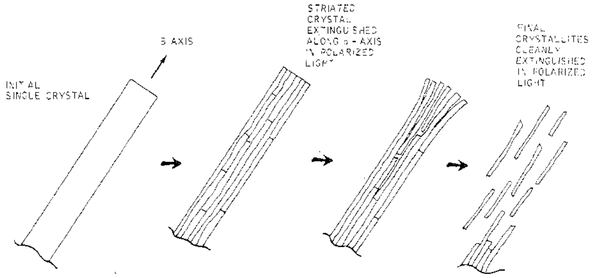
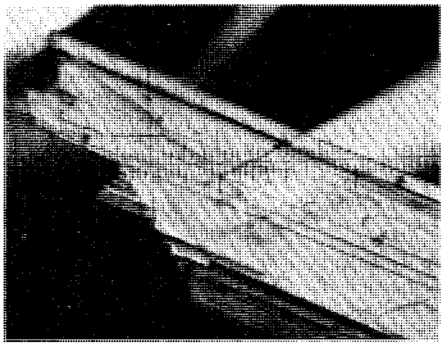
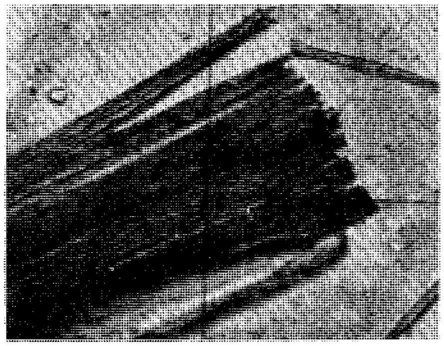


Figure 3. Schematic representation of the reaction of a single crystal of MX_3 with *n*-butyllithium.



SINGLE CRYSTAL OF HfS_3
TRANSMITTED POLARIZED LIGHT



Li_3HfS_3 TRANSMITTED LIGHT
320X

Figure 4. Reaction of *n*-butyllithium with a single crystal of HfS_3.

Table II. X-Ray Powder Diffraction Pattern of Li_3TiS_3[a,b]

hkl	I/I_0	d_{obsd}	d_{calcd}
100	40	11.8	11.0
001	80	9.1	9.0
$10\bar{1}$	40	7.2	7.5
101	60	6.4 b	6.6
$20\bar{1}$	40	5.00	5.02
002	60	4.51	4.52
010	60	3.47	3.46
110	20	3.30	3.30
003	20	3.01	3.01
210	40	2.940	2.932
$11\bar{2}$	60	2.722	2.721
212/401	100	2.555 vb	2.547 2.537
212	10	2.380	2.380
$31\bar{2}$	10	2.294	2.295
204	20	2.005	1.994
600	80	1.834	1.835
114	40	1.829	1.829
315	20	1.543	1.539
123/023	20	1.449	1.501
802	5	1.269	1.269

[a] Debye-Scherrer data; Cu Kα radiation. [b] $a = 11.1$ (1) Å, $b = 3.46$ (1) Å, $c = 9.12$ (2) Å, $\beta = 98.0$ (2)°.

Table III. X-Ray Powder Diffraction Pattern Li_3ZrS_3[a]

hkl	I/I_0	d_{obsd}	d_{calcd}
001	85	9.1	9.1
101	45	6.4	6.5
002	45	4.56	4.54
$10\bar{3}$/003	15	3.04	3.06/3.03
212	100	2.627	2.627
$31\bar{3}$	60	1.850	1.851

[a] $a = 11.2$ (1) Å, $b = 3.59$ (1) Å, $c = 9.22$ (2) Å, $\beta = 100.0$ (2)°.

Table IV. X-Ray Powder Diffraction Pattern Li_3ZrSe_3[a]

hkl	I/I_0	d_{obsd}	d_{calcd}
001	100	9.60	9.56
101	30	6.90	6.88
002	60	4.80	4.78
300	30	3.88	3.89
$10\bar{3}$	50	3.20	3.21
210	20	3.15	3.16
$21\bar{2}$	30	2.760	2.747
600/114	20	1.948b	1.947/1.944
$12\bar{3}$/023	20	1.620	1.622/1.619

[a] $a = 11.8$ (1) Å, $b = 3.76$ (1) Å, $c = 9.68$ (2) Å, $\beta = 99.1$ (1)°.

Table V. X-Ray Powder Diffraction Pattern Li_3HfS_3[a]

hkl	I/I_0	d_{obsd}	d_{calcd}
001	100	9.2	9.1
101	20	6.5	6.7
200	20	6.0	5.9
002	70	4.57	4.55
$10\bar{3}$/003	20	3.05	3.07/3.03
$21\bar{2}/31\bar{1}$	50	2.620	2.632/2.631
$10\bar{5}$	20	1.847	1.847

[a] $a = 12.1$ (1) Å, $b = 3.52$ (1) Å, $c = 9.42$ (2) Å, $\beta = 100$ (1)°.

Table VI. X-Ray Powder Diffraction Pattern Li_3HfSe_3[a]

hkl	I/I_0	d_{obsd}	d_{calcd}
100	5	11.6	11.3
001	10	9.50	9.42
101	10	6.70	6.79
002	10	4.76	4.72
300	40	3.77	3.78
$21\bar{1}$	100	3.00	3.00
$11\bar{2}$/211	10	2.901	2.891/2.887
310	10	2.657	2.652
$50\bar{2}$	20	2.178	2.169
204	20	2.069	2.075
$11\bar{4}$/014	20	1.995	2.003/1.992
$220/50\bar{4}$	20	1.763	1.767/1.766
115/222	10	1.635	1.634/1.631
405	10	1.478	1.476
124/600	10	1.426b	1.432/1.418

[a] $a = 11.5$ (1) Å, $b = 3.71$ (1) Å, $c = 9.52$ (2) Å, $\beta = 98.1$ (1)°.

as seen in Figure 4. Never was any material seen to dissolve or precipitate from solution. This was seen to be a general phenomenon with all the trichalcogenides investigated. From this, it can be concluded that the product formed is a ternary compound because no second phase was seen and because the crystallinity of the product was retained. It is also observed that larger crystals break up along the needle axis into smaller crystals because of the expansion of the lattice required to incorporate the three lithium atoms (as is consistent with later X-ray data). The three lithium atoms are incorporated into the existing structure without severe disruption of that structure and may be classified as "permutoidal" or topochemical reactions. These terms are defined by Wells[8] as reactions "in which a substance reacts in a liquid or gaseous medium without breakdown of its structure, some part of the structural scheme of the original solid remaining intact." A further demonstration of the flexibility of this structure was noted when a sample of Li_3TiS_3 was placed in an optical cell and several drops of water were added. The resulting reaction was observed optically. Gas bubbles were seen forming and individual crystallites were seen to change from their characteristic red-orange semitransparent state to completely transparent colorless needle-like crystals. Probably the Li_3MX_3 incorporates water into the lattice, again topochemically. These observations provide excellent examples of macroscopic manifestation of microscopic processes such as described by Paul and Curtin.[9]

X-Ray Diffraction. The observed powder patterns for Li_3MX_3 compounds appear in Tables II–VII. All of these patterns are indexable on an expanded trichalcogenide lattice

Table VII. X-Ray Powder Diffraction Pattern Li_3NbSe_3[a,b]

hkl	I/I_0	d_{obsd}	d_{calcd}
$20\bar{2}$	40	4.94	5.07
301	60	4.75	4.78
202	40	4.49	4.44
$30\bar{2}$	80	4.39	4.32
010	40	3.51	3.48
011	60	3.34	3.33
$11\bar{1}$	20	3.28	3.29
$21\bar{2}$	80	2.867	2.869
$20\bar{4}$	100	2.819	2.827
$60\bar{2}$	40	2.677	6.673
113	40	2.477	2.503
304	60	2.412	2.410
503	40	2.365	2.361
$30\bar{5}$	40	2.231	2.228
014	40	2.206	2.206
$114/60\bar{4}$	20	2.166	2.160
611	10	2.103	2.103
305	40	2.016	2.017
314	20	1.980	1.980
$80\bar{3}$	20	1.966	1.963
$810/70\bar{5}$	20	1.793	1.801 1.787
306	80	1.728	1.729
$22\bar{1}$	40	1.691	1.692
$91\bar{2}$	40	1.637	1.639
804	10	1.590	1.590
$322/51\bar{6}$	10	1.577	1.578 1.576
$32\bar{3}$	20	1.547	1.547
$101\bar{1}$	20	1.528	1.528

[a] Debye-Scherrer; Cu Kα radiation. Additional low angle lines appeared in diffractometer trace which were indexed as 100, 001, 101, 201, 002, and 102. [b] $a = 17.1$ (1) Å, $b = 3.48$ (2) Å, $c = 11.5$ (1) Å, $\beta = 98.1$ (2)°.

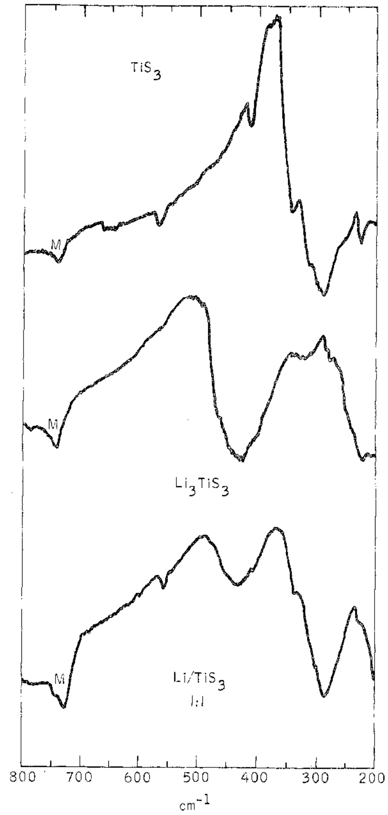


Figure 5. Infrared spectra of TiS_3, Li_3TiS_3, and 1:1 Li/TiS_3 (M = Marcol vibration).

with a doubled *a* axis (except $NbSe_3$ which has a simple expanded lattice). The new lattice parameters and expansions are included in Table VIII. In general, the *b* axis and β remain constant and the *a* axis and *c* axis expand. Based upon the best data (Li_3TiS_3 Debye–Scherrer photograph) the expansion for $TiS_3 \rightarrow Li_3TiS_3$ in the *a* direction is 1.2 Å and in the *c* direction is 0.35 Å. Poorly resolved diffractometer data made expansions less certain for the remaining Li_3MX_3. Nevertheless, it can be seen that this is a general phenomenon for the group 4B materials. The question to be answered is how are the Li incorporated into the lattice. From the optical observations and from the fact that the *b* axis does not expand we can conclude that the infinite chains of distorted trigonal prisms remain intact. We further conclude from the expansions of the *a* and *c* parameters that the lithium atoms in some manner surround these infinite chains. We cannot at this time be conclusive about the manner in which this occurs. However, one way in which this can happen is indicated in Figure 1. The trigonal prismatic chains rearrange slightly but remain intact and are surrounded by three lithium atoms. The trigonal prisms may tend to become more octahedral in the group 4B compounds after breaking of the polychalcogenide bond. The proposed structure for Li_3TiS_3 has an expansion of 1.2 Å along the double *a* axis which is approximately 1Li^+ diameter of 1.18 Å[10] (doubling not shown in Figure 1) and a filling of the van der Waals gap with lithium. We cannot say without further crystallographic work what the precise arrangement of the lithium atoms and the trigonal prismatic chains is. The proposed structure can also explain the observed rapid uptake of two Li and the slower uptake of the third in Li_3TiS_3. The first two move rapidly down the chain axis in the van der Waals gaps breaking the polysulfide bonds. They must then diffuse to the center before taking up a third. For Li_3NbSe_3 it appears that no multiplication of any axis occurs, but only expansion of the existing axes. This indicates that the rearrangement required for incorporation of three Li into the lattice is less severe than in the group 4B compounds. This probably reflects the tendency of the group 5B metals toward trigonal prismatic coordination which allows lattice expansion and change of oxidation state without change of coordination about the metal atoms.

Infrared Spectroscopy. Perrin et al.[11] studied the infrared and Raman spectra of the trichalcogenides and related compounds. For MX_3 (symmetry C_{2v}) there are four M–X one X–X ir-active vibrations. Perrin et al. have assigned the vibrations for TiS_3 and ZrS_3 which agree well with our observations. We have also tentatively assigned the vibrations for HfS_3 (similar to ZrS_3) and $ZrSe_3$ and $HfSe_3$. In the latter

Table VIII. Lattice Expansion of Li_3MX_3[a,b]

	$2a_0$, Å[b]	b_0, Å[b]	c_0, Å[b]	β_0, deg[b]	*a*, Å	*b*, Å	*c*, Å	β, deg	Δa, Å	Δb, Å	Δc, Å	$\Delta\beta$
Li_3TiS_3	9.92	3.40	8.78	97.3	11.1	3.46	9.12	98.0	1.2	+0.06	0.34	0.7
Li_3ZrS_3	10.25	3.62	8.98	97.3	11.2	3.59	9.22	100	1.0	−0.03	0.24	2.7
Li_3ZrSe_3	10.82	3.75	9.44	97.5	11.8	3.76	9.68	99.1	1.0	+0.01	0.24	1.6
Li_3HfS_3	10.18	3.60	8.97	97.4	12.1	3.52	9.24	100	1.9	−0.08	0.27	2.6
Li_3HfSe_3	10.78	3.72	9.43	97.8	11.5	3.71	9.52	98.1	0.7	−0.01	0.09	0.7
Li_3NbSe_3	15.63	3.48	10.06	109.3	17.0	3.48	11.5	98.1	1.4	0.00	1.4	12.7

[a] a_0, b_0, c_0, β_0 lattice parameters of unlithiated trichalcogenides from L. Brattas and A. Kjekshus, *Acta Chem. Scand.*, 26, 3441 (1972), except $NbSe_3$ from A. Meerschant and J. Rouxel, *J. Less-Common Met.*, 39, 197 (1975). [b] Lattice parameters were calculated from least-squares fits to the observed *d* values.

Table IX. Ir (cm^{-1}) of the Trichalcogenides

Peak assignment	TiS_3^{a}	ZrS_3^{a}	HfS_3	$ZrSe_3$	$HfSe_3$
α X–X	560 w	529 w	548 w	280 m	300 w
β_1 M–X	400 w	365 w	352 m, 343 vw	303 m	328 w
β_2 M–X	335 m	315 s	278 s	253 w	253 vw
β_3 M–X	285 vs	250 vs	240 s	230 m	232 w
β_4 M–X	220 w	225 vw	220 w		

^{a} Assignments for TiS_3 and ZrS_3 were made in ref 9.

cases the polyselenide bond vibration should move down to lower energies according to the relation[12]

$$1.862 = \frac{\nu_{S\text{-}S}}{\nu_{Se\text{-}Se}} = \frac{\sqrt{K_{S\text{-}S}/K_{Se\text{-}Se}}}{\sqrt{m_S/m_{Se}}} \qquad \begin{aligned} K_{S\text{-}S} &= 2.69 \\ K_{Se\text{-}Se} &= 1.91 \\ m_S &= 32.06 \\ m_{Se} &= 78.96 \end{aligned}$$

Here, K is the spring constant for the elements[12] and m is the respective chalcogenide mass. When the polyselenide bonds are scaled in this manner, we obtain 283 and 294 cm^{-1} for the $ZrSe_3$ and $HfSe_3$ S–S vibrations. These agree well with observed values of 280 and 300 cm^{-1} for the two compounds and assignment of the polyselenide bond is made on this basis. All other bands appearing in the selenides are assigned to M–Se vibrations and no attempt to scale these from the sulfides was made because of the poorly resolved spectra. The observed trichalcogenide vibrations are indicated in Table IX.

The extremely pyrophoric nature of the lithiated materials made preparation and characterization of lithiated samples difficult, especially in the case of the Zr compounds.

In Li_3TiS_3 (Figure 5) we note that the polysulfide peak at 560 cm^{-1} has disappeared and a strong wide peak appears at 425 cm^{-1} which was not present in the starting TiS_3. The very strong peak at 285 cm^{-1} is not present in the lithiated product. The spectrum of the Li_3TiS_3 is consistent with the observations made in previous sections. The polysulfide bond is broken on incorporation of lithium and the new structure contains two types of bonds Li–S and Ti–S. We can assign the peak at 425 cm^{-1} as a Li–S bond vibration (in lithium sulfide this vibration is a strong broad peak centering near 465 cm^{-1}). The other peak at 225 cm^{-1} is probably a Ti–S stretch such as found in TiS_2 at 220 cm^{-1} [13] and is present in the starting TiS_3. The presence of only two peaks in the product suggests a higher symmetry than in the starting materials. The infrared of TiS_3 when only 1 equiv of *n*-butyllithium was added includes peaks from both Li_3TiS_3 and TiS_3 indicating a mixture of these two materials and not the formation of a homogeneous single phase (see Figure 5).[14] The spectra of the remaining lithiated trichalcogenides show the same general trend, but it is much more difficult to obtain good spectra because of the extreme air sensitivity and the poor resolution of the triselenide spectra. In Li_3ZrS_3 and Li_3HfS_3 the vibrations appear at 430 and 420, and 254 and 270 cm^{-1}, respectively, but a third vibration at 300 cm^{-1} appears in both.

Conclusion

We may summarize the results of this work by stating that in general the reaction of *n*-butyllithium with the transition metal trichalcogenides yields a ternary phase of the type Li_3MX_3. This reaction occurs with incorporation of lithium into the existing structure, part of which remains intact. The chains of TiS_6 are essentially undisturbed during the inclusion with lithium occupying surrounding sites and forcing an expansion normal to the chains. This expansion causes a slight rearrangement of the basic structure with rupture of the polychalcogenide bonds of the original structure. The rearrangement in the group 5B trichalcogenides may be less severe than that in the group 4B compounds, probably because of the group 4B metal's preference for octahedral coordination.

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Registry No. Li_3TiS_3, 55886-05-0; Li_3ZrS_3, 55886-06-1; Li_3ZrSe_3, 55886-07-2; Li_3HfS_3, 55886-01-6; Li_3HfSe_3, 55886-02-7; Li_3NbS_3, 55886-03-8; Li_3NbSe_3, 55886-04-9; TiS_3, 12423-80-2; ZrS_3, 12166-31-3; $ZrSe_3$, 12166-53-9; HfS_3, 39293-73-7; $HfSe_3$, 39293-74-8; NbS_3, 12316-04-0; $NbSe_3$, 12034-78-5; *n*-butyllithium, 109-72-8.

References and Notes

(1) Presented at the 169th National Meeting of the American Chemical Society, Philadelphia, Pa., April 6–11, 1975.
(2) M. B. Dines, *Mater. Res. Bull.*, **10**, 287 (1975).
(3) (a) V. W. Kronert and K. Plieth, *Z. Anorg. Allg. Chem.*, **336**, 207 (1965); (b) E. Bjerkelund and A. Kjekshus, *Acta Chem. Scand.*, **19**, 701 (1965).
(4) A. Meerschant and J. Rouxel, *J. Less-Common Met.*, **39**, 197 (1975).
(5) H. Haraldsen, A. Kjekshus, E. Rost, and A. Steffansen, *Acta Chem. Scand.*, **17**, 1283 (1963).
(6) M. S. Whittingham and F. R. Gamble, *Mater. Res. Bull.*, **10**, 363 (1975).
(7) E. Bayer and W. Rudorff, *Z. Naturforsch.*, **276**, 1336 (1972).
(8) A. F. Wells, "Structural Inorganic Chemistry", 3rd ed, Oxford at the Clarendon Press, 1967, p 537.
(9) I. C. Paul and D. V. Curtin, *Science*, **187**, 19, 4171 (1975).
(10) R. D. Shannon and C. T. Prewitt, *Acta Crystallogr., Sect. B*, **25**, 925 (1969).
(11) C. Perrin, A. Perrin, and J. Prigent, *Bull. Soc. Chim. Fr.*, **8**, 3086 (1972).
(12) G. R. Somayajulu, *J. Chem. Phys.*, **28**, 814 (1958).
(13) J. E. Smith, Jr., M. I. Nathan, M. W. Shafer, and J. B. Torrance, *Mater. Res. Bull.*, **9**, 1306 (1974).
(14) The nature of this two-phase region has been discussed in detail in a paper presented at the 147th Meeting of the Electrochemical Society held in Toronto, Canada, May 11–16, 1975, and will be the subject of a future paper.