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Organometallic Intercalates of the Layered Transition-Metal Dichalcogenides TaS_2 and ZrS_2

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Substituted cobaltocenes $(RC_5H_4)_2Co$ (R = Me, *i*-Pr, and *n*-Bu) have been intercalated into the layered dichalcogenides TaS_2 and ZrS_2 by direct reaction of toluene solutions of the organometallic compounds and the solid disulfides. Intercalates of TaS_2 have also been prepared by ion exchange of the hydrated sodium intercalate with organometallic cations in aqueous solution. Lattice expansions of the host disulfides on intercalation have been determined by powder X-ray diffraction and are discussed in relation to the orientation of the organometallic cation between the layers. Some chemical reactions of the intercalates and some ion-exchange experiments in nonaqueous solvents are described.

Introduction

Layered transition-metal dichalcogenides may act as host lattices and react with a variety of guest atoms or molecules to give intercalation compounds in which the guest is inserted between the host layers.[1,2] Interest in these materials has arisen for such diverse reasons as the observation that the superconducting transition temperature of some hosts increases on intercalation of amines[3] and the use of alkali metal intercalation reactions such as Li/TiS_2 in secondary battery systems.[4] Chemical applications of intercalates of other layered materials have been demonstrated. Graphite/bromine and graphite/bisulfate are useful reagents in organic syntheses[5] and the catalytic hydrogenation properties of $Rh(PPh_3)_x^+$ are modified on intercalation into silicates.[6]

The observation by Dines[7] that cobaltocene and chromocene could be directly intercalated into most layered dichalcogenides to give compounds such as $\{[(\eta\text{-}C_5H_5)_2Co]_{1/4}TaS_2\}$ prompted us to examine more generally the synthesis and potential applications of such organometallic intercalated systems as models for heterogeneous catalysis. In a preliminary report[8] we described the synthesis of several new intercalation compounds of organometallic compounds and the host ZrS_2. These data are summarized in Table I. All of the intercalates were prepared by direct reaction of ZrS_2 and the neutral organometallic molecule in toluene solution. On the basis of this study three preliminary criteria for direct intercalation were established. All of the organometallic compounds which were successfully intercalated have sandwich structures with parallel carbocyclic rings, have first ionization potentials less than 6.2 eV, and form cations which are stable to isolation. Experimental details of this work not given in the preliminary communication are included in the Experimental Section.

In this paper, we report an extension of this work to other layered dichalcogenide host lattices and organometallic compounds. In particular, we have examined in more detail steric effects associated with the organometallic compound on the direct intercalation reaction and on the orientation of the guest molecule between the layers. We have also investigated ion-exchange reactions as a more general synthetic route to new intercalation compounds.

Table I. Organometallic Intercalates of ZrS_2

guest	stoichiometry $(x)^a$	c, Å	lattice expansion, Å
$(\eta\text{-}C_6H_6)_2Mo$	0.16	34.93 (2)	5.81 (1)
$(\eta\text{-}C_6H_5CH_3)_2Mo$	0.13	34.90 (4)	5.80 (2)
$(\eta\text{-}C_6H_3(CH_3)_3)_2Mo$	0.08	34.83 (4)	5.78 (2)
$(\eta\text{-}C_6H_6)_2Cr$	0.16	35.20 (2)	5.90 (1)
$(\eta\text{-}C_5H_5)_2Cr$	0.25	34.31 (2)	5.61 (1)
$(\eta\text{-}C_6H_6)(\eta\text{-}C_5H_5)Cr$	0.24	35.70 (2)	6.07 (1)
$(\eta\text{-}C_7H_7)(\eta\text{-}C_5H_5)Cr$	0.25	36.0 (2)	6.17 (7)
$(\eta\text{-}C_8H_8)(\eta\text{-}C_5H_5)Ti$	0.23	36.69 (1)	6.40 (1)

^{a} x in $(\text{guest})_xZrS_2$.

Experimental Section

Powder X-ray diffraction data were obtained using a Philips wide-angle goniometer and Cu Kα radiation. Lattice parameters were obtained by least-squares analysis of the peak positions. The compounds $M(\eta\text{-}C_6H_6)_2$, M = Cr, Mo,[9,10] $[Fe(\eta\text{-}C_5H_5)(\eta\text{-}C_6H_6)]PF_6$,[11] and $Co(\eta\text{-}MeC_5H_4)_2$[12] were prepared as described previously. The compounds $Co(\eta\text{-}RC_5H_4)_2$, R = *i*-Pr or *n*-Bu, were prepared as described below.

Synthesis of Metal Dichalcogenides. Most of the dichalcogenides were synthesized from the elements. The metals were obtained "Specpure" from Johnson Matthey Chemicals and sulfur and selenium from BDH. The metal (typically 10 g) and the chalcogen (1% excess over the stoichiometric amount) were placed in a silica tube (ca. 25–50 cm^3) and sealed under vacuum. The silica tubes were baked out at 900 °C prior to use. Reaction conditions for the various preparations are given in Table II. Excess chalcogen was removed by vacuum sublimation. Sample purity was checked by X-ray diffraction and thermogravimetric analysis.

Direct Synthesis of Intercalates. A typical reaction is described. The pure transition-metal dichalcogenide was ground and sieved to 200 mesh and placed in a dry Pyrex ampule. A solution of the sandwich compound in dry toluene was added under nitrogen and the ampule sealed under vacuum. The ampule was heated at 130 °C for 3 days and opened under nitrogen, and the solid separated. The solid was washed several times with dry degassed toluene and dried under vacuum. The reaction was assumed complete when no lines due to starting material were observed in the X-ray powder diffraction pattern.

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Table II. Preparation of the Transition-Metal Chalcogenides[a]

compd	A	B	C	D
TiS_2	wire	900 °C, 3 days	+excess S, 550 °C 3 days	1T gold
ZrS_2[b]	wire	900 °C, 3 days	I_2 VPT[c]	1T dk blue
HfS_2	sponge	S, VPT 900–800 °C		1T red
NbS_2	wire	900 °C, 10 days	quenched	2H silver
TaS_2[d]	wire	900 °C, 30 days	S, VPT 950–900 °C, 300 °C, 60 days	1T gold, 2H black
$TiSe_2$	wire	650 °C, 3 days		1T violet
$ZrSe_2$	wire	650 °C, 3 days		1T green
VSe_2	coarse powder	650 °C, 3 days		1T black
$NbSe_2$	wire	900 °C, 7 days	slow cool	2H silver
$TaSe_2$	wire	900 °C, 7 days	slow cool	3R silver

[a] Key: A, physical form of the metal used; B, reaction conditions; C, final treatment to obtain a pure phase; D, resulting polytype and its appearance. [b] Later samples of ZrS_2 were prepared by thermal decomposition of ZrS_3. [c] VPT = vapor phase transport. [d] Later samples of 2H TaS_2 were prepared by the following method.[13] Tantalum wire and a small excess of sulfur over the stoichiometric amount were heated at 900 °C for 7 days. The temperature was started at 450 °C and raised to 900 °C at 50 °C/day. The tube was then opened and a "pinch" of Ta wire added (a few mg/10 g of starting Ta). The mixture was reheated at 900 °C and then cooled slowly over 7 days to 500 °C.

Table III. Organometallic Intercalates of 1T TaS_2, ZrS_2, $ZrSe_2$, VSe_2

host	organometallic	stoichiometry (x)[c]	a, Å	c, Å	Δc, Å
1T TaS_2	1,1′-dimethylcobaltocene[a]	0.21	3.33 (1)	34.78 (3)	5.68
	1,1′-diisopropylcobaltocene[a]	0.17	3.32 (1)	36.15 (3)	6.18
	1,1′-di-*n*-butylcobaltocene[a]	0.13	3.37 (1)	34.31 (3)	5.53
	1,1′-di-*tert*-butylcobaltocene[a]	no intercalation			
	diindenylcobaltocene[a]	no intercalation			
	bis(η-benzene)chromium[a]	no intercalation			
	bis(η-benzene)molybdenum[a]	no intercalation			
	1,1′-dimethylcobaltocenium iodide[b]	0.14			
	1,1′-diisopropylcobaltocenium iodide[b]	0.07 (less crystalline)			
	1,1′-di-*n*-butylcobaltocenium iodide[b]	0.05 (partial intercalation)			
	1,1′-di-*tert*-butylcobaltocenium iodide[b]	no intercalation			
	bis(η-benzene)chromium iodide[b]	0.13	3.36 (1)	35.85 (3)	6.04
	bis(η-benzene)molybdenum iodide[b]	0.15	3.38 (1)	35.68 (3)	5.99
	(η^5-cyclopentadienyl)(η-benzene)iron hexafluorophosphate[b]	0.16	3.38 (1)	34.90 (3)	5.72
	cobaltocenium iodide[b]	0.20	3.39 (1)	34.15 (3)	5.50
ZrS_2	1,1′-dimethylcobaltocene[a]	0.25	3.70 (2)	33.5 (1)	5.34
	1,1′-diisopropylcobaltocene[a]	0.15	3.65 (2)	34.7 (1)	5.74
	1,1′-di-*n*-butylcobaltocene[a]	0.13	3.67 (2)	33.5 (1)	5.34
$ZrSe_2$	cobaltocene[a]	0.25			
VSe_2	cobaltocene[a]	0.25			

[a] Prepared by direct reaction. [b] Prepared by ion exchange. [c] The stoichiometry x is calculated from the C, H analysis.

The stoichiometry of the intercalate was determined by C, H (and occasionally M, S) analysis of several samples.

Cation-Exchange Synthesis of Intercalates. A typical procedure is described. $Na_{0.3}(H_2O)_yTaS_2$ (0.2 g) was suspended in a dilute aqueous solution of the organometallic salt (0.2 g) containing sodium bicarbonate and stirred at room temperature for 15 h. The solid was separated, washed with water, and dried under vacuum. The intercalate was characterized as described for the direct method.

1,1′-Di-*tert*-butylcobaltocene. Dimethylfulvene (8.5 g) in diethyl ether (50 cm^3) was treated with 2 M methyllithium in ether (40 cm^3). The resulting white solid was filtered, washed with ether, and then dissolved in dry tetrahydrofuran. Hexaamminecobalt(II) chloride (9.3 g) was added and the mixture refluxed for 6 h. The mixture was filtered and the solvent removed under reduced pressure. The dark oily residue was distilled at 10^{-1} Torr, 180 °C, to give dark brown crystals, ca. 65%. Anal. Calcd for the PF_6^- derivative: C, 48.4; H, 5.8. Found: C, 48.2; H, 6.2.

The salts $[Co(\eta\text{-}RC_5H_4)]^+I^-$, R = H, Me, *i*-Pr, *t*-Bu, were prepared by the slow addition of a stoichiometric amount of iodine to the pure neutral cobaltocenes. PF_6^- derivatives were prepared by addition of NH_4PF_6 to aqueous solutions of the iodide salts.

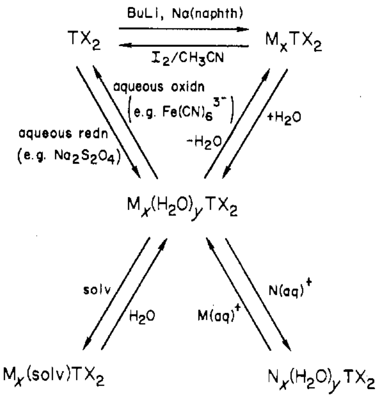
1,1′-Diisopropylcobaltocene and 1,1′-Di-*n*-butylcobaltocene. Hexaamminecobalt(II) chloride (10 g) was treated with an excess (10%) of sodium isopropylcyclopentadienide[14] in tetrahydrofuran. The mixture was heated under reflux for 12 h. The solvent was removed under reduced pressure. The pure product was isolated from the residue by distillation (170 °C (10^{-1} Torr)) giving a dark brown oil, ca. 60%. A portion of this oil was treated with iodine giving the yellow-green iodide salt. The salt was dissolved in water and the aqueous extract was treated with aqueous ammonium hexafluorophosphate. The resulting yellow-green precipitate was recrystallized from acetone–water and dried under reduced pressure. Anal. Calcd for $C_{16}H_{22}CoF_6P$: C, 45.9; H, 5.3. Found: C, 45.7; H, 5.5.

The 1,1′-di-*n*-butylcobaltocene was similarly prepared using sodium *n*-butylcyclopentadienide.[15] The product was isolated as a dark brown oil and was characterized by conversion to the 1,1′-di-*n*-butylcobaltocenium hexafluorophosphate as described for the isopropyl analogue. Anal. Calcd for $C_{18}H_{26}CoF_6P$: C, 48.4; H, 5.8. Found: C, 47.1; H, 6.2.

Results

Ion-Exchange Reactions. Alkali metal and quaternary ammonium cation intercalates of the dichalcogenides have been shown to undergo several types of chemical reactions which are summarized in Scheme I. For organometallic intercalation, the direct reaction in which the neutral organometallic compound acts as its own reducing agent is analogous to reactions with BuLi or alkali metal naphthalides. However, many organometallic cations are known where the corresponding neutral species do not exist, e.g. $[(\eta\text{-}C_5H_5)(\eta\text{-}C_6H_6)Fe]^+$. Ion-exchange reactions (see for example Schollhorn et al.[16]) and electrointercalation are potentially more general synthetic routes. Further, the kinetics of direct intercalation reactions involving bulky guest species are often slow, but reaction rates may be enhanced by preintercalating a small cation such as Na^+ which separates the host layers followed by ion exchange with the large cation. A major difficulty with this approach is the stability of the host lattice to hydrolysis. 1T TaS_2 is, however, stable in slightly alkaline aqueous solution, and we previously reported[8] the synthesis

Scheme I



of $\{[Cr(\eta\text{-}C_6H_6)_2]_{0.14}TaS_2\}$ by ion exchange of $K_{1/3}(H_2O)_{2/3}TaS_2$ with $\{[Cr(\eta\text{-}C_6H_6)_2]^+\}$. This intercalate could not be prepared by direct reaction of $(\eta\text{-}C_6H_6)_2Cr$ and TaS_2. Several new compounds have been prepared from the sodium intercalate and are given in Table III. Table III also includes some intercalates previously prepared by direct reaction but prepared here by ion exchange, e.g., $\{[Co(\eta\text{-}C_5H_5)_2]_{0.2}TaS_2\}$. Even under slightly basic conditions, some hydrolysis of the TaS_2 host probably occurs and this may account for the slightly lower stoichiometrics of ion-exchange compounds compared with those of the analogous materials prepared by direct reaction.

To overcome this problem some ion-exchange reactions were attempted in nonaqueous solvents. Cation exchange between $Na_{0.3}(H_2O)_yTaS_2$ and $[Co(\eta\text{-}C_5H_5)_2]^+I^-$ was successful in both dry methanol and ethanol but the rate of exchange was slow, particularly in ethanol. No exchange was observed in dry tetrahydrofuran containing 18-crown-6 ether to solubilize the sodium ions.

Direct Reactions. New organometallic intercalates of 1T TaS_2, ZrS_2, $ZrSe_2$, and VSe_2 prepared by direct reaction are given in Table III. The intercalates were all black crystalline solids which slowly decompose in air. Several chemical reactions of these compounds were investigated. Treatment of $[Co(\eta\text{-}C_5H_5)_2]_{1/4}TaS_2$ (I) with an aqueous solution of Na^+ at 25 °C for 7 days gave no indication of ion exchange either in formation of a sodium intercalate or in release of $Co(\eta\text{-}C_5H_5)_2^+$ ions into the solution. However, treatment with water in a sealed tube at 130 °C for 3 days resulted in release of cobaltocenium ions into solution and the formation of TaS_2 as shown by X-ray powder diffraction. Hydrogen gas was also identified as a product. The overall reaction may be written $[Co(\eta\text{-}C_5H_5)_2]_{1/4}TaS_2 + {}^1/_4H_2O \rightarrow {}^1/_4Co(\eta\text{-}C_5H_5)_2^+ + {}^1/_4OH^- + TaS_2 + {}^1/_8H_2$. As expected I reacts rapidly with aqueous iodine to give $Co(\eta\text{-}C_5H_5)_2^+I^-$ and TaS_2. The decomposition and oxidation behavior of two materials, $[Cr(\eta\text{-}C_6H_6)_2]_{0.15}ZrS_2$ and $[Mo(\eta\text{-}C_6H_6)_2]_{0.16}ZrS_2$, was investigated by thermogravimetric analysis (Figure 1). Both compounds show an initial weight loss corresponding to loss of the benzene rings followed by oxidation of Mo to MoO_3 and Cr to Cr_2O_3 and subsequent oxidation of the host lattice to ZrO_2. The molybdenum compound shows a high-temperature weight loss corresponding to MoO_3 volatilization. The thermogravimetric analysis of ZrS_2 is shown for comparison. X-ray diffraction studies indicated that the initial benzene ring loss did not occur topochemically but was associated with deintercalation of the organometallic compound. The stoichiometries of the starting materials determined from the TGA were in good agreement with those determined by other methods.

We have been unable to obtain intercalation compounds by direct reaction between $M(\eta\text{-}C_6H_6)_2$ (M = Cr, Mo) and the hosts TiS_2, $TiSe_2$, $ZrSe_2$, HfS_2, VSe_2, NbS_2, TaS_2 (1T and 2H), $TaSe_2$, MoS_2, V_2O_5, MoO_3, and graphite. Preliminary experiments have shown that MoO_3 and V_2O_5 both react with cobaltocene to give intercalation compounds. For example, a black solid of composition $[Co(\eta\text{-}C_5H_5)_2]_{0.2}MoO_3$ is obtained by direct reaction of MoO_3 with cobaltocene for 3 days at 130 °C. The X-ray pattern is complex, but additional low-angle reflections are present indicating an enlarged unit cell.

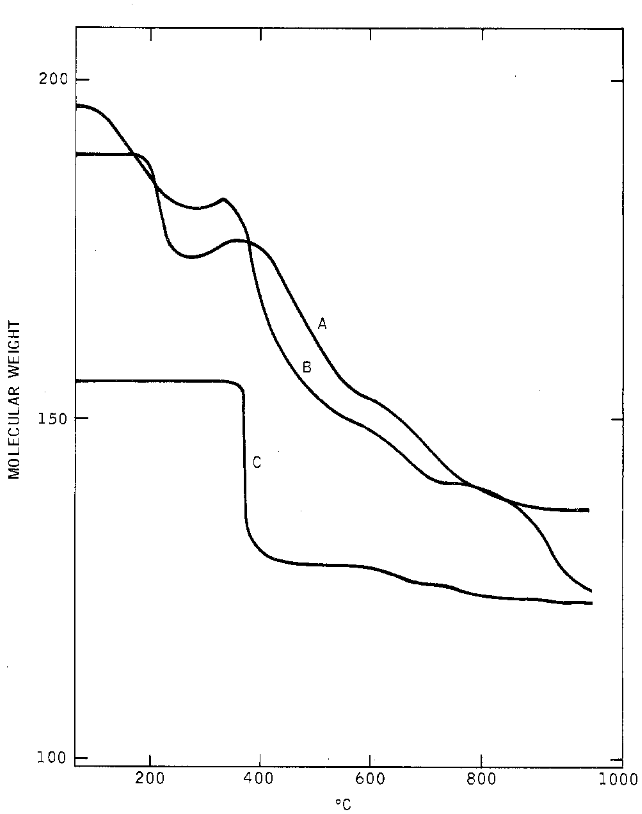


Figure 1. Thermogravimetric decomposition and oxidation of (A) $[(\eta\text{-}C_6H_6)_2Cr]_{0.16}ZrS_2$, (B) $[(\eta\text{-}C_6H_6)_2Mo]_{0.16}ZrS_2$, and (C) ZrS_2.

Discussion

X-ray diffraction patterns of all the organometallic intercalation compounds prepared in this and previous work could be indexed on the basis of a hexagonal unit cell with the *c* axis perpendicular to the layers. The *c* axis is tripled compared with the *c* axis of the 1T or 2H host lattices, but all of the (00*l*) reflections have $l = 3n$ indicating that the separation between successive host layers is *c*/3. A typical diffraction pattern for an intercalate prepared by direct reaction is shown in Figure 2, and the indexing and observed and calculated *d* spacings are given in Table IV. Intercalates prepared by ion exchange gave broader diffraction patterns. The tripled *c* axis does not imply that the stacking sequence of the host layers has transformed into a rhombohedral polytype such as found for $LiZrS_2$ since the mixed reflections do not obey rhombohedral absences; e.g., (106) and (1,0,12) are strong in the diffraction pattern shown. The detailed structural interpretation of the tripled *c* axis is not clear but we note that a similar effect is observed for $LiHfS_2$.[17] From the measured *c* axis of the intercalates and the *c* axis of the host materials, the lattice expansion which occurs on intercalation of the organometallic compound into the van der Waals gap of the host lattice may be obtained. A comparison of this lattice expansion with the estimated van der Waals dimensions of the organometallic molecule gives information about the orientation of the guest between the layers. Lattice expansions calculated in this way are given in Tables I and III; *c*-axis spacings for ZrS_2, 1T TaS_2, $ZrSe_2$, and VSe_2 were

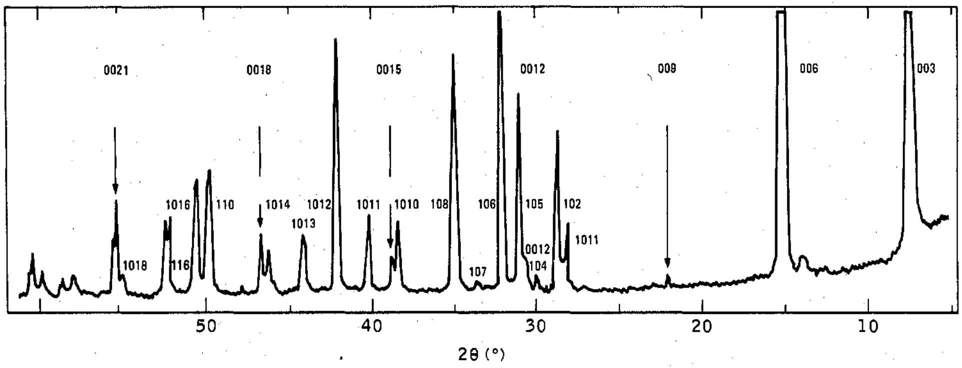


Figure 2. X-ray powder diffraction pattern of $[(\eta\text{-}C_6H_6)_2Mo]_{0.16}ZrS_2$.

Table IV. X-Ray Powder Data for $[(\eta^6\text{-}C_6H_6)_2Mo]_{0.16}ZrS_2$

hkl	*d*(obsd), Å	*d*(calcd), Å	I^b
003	11.56	11.64	*a*
006	5.79	5.82	*a*
009	3.869	3.881	6
100	3.166	3.160	29
102	3.106	3.110	66
104	2.965	2.971	6
0,0,12	2.907	2.911	7
105	2.875	2.879	79
106	2.779	2.777	*a*
107	2.668	2.670	4
108	2.557	2.560	95
1,0,10	2.341	2.343	33
0,0,15	2.323	2.329	16
1,0,11	2.238	2.240	32
1,0,12	2.141	2.141	100
1,0,13	2.047	2.044	22
1,0,14	1.957	1.958	17
0,0,18	1.941	1.941	24
110	1.824	1.825	50
1,0,16	1.797	1.796	46
116	1.741	1.741	32
0,0,21	1.661	1.663	6
1,0,18	1.654	1.654	39
1,0,19	1.586	1.589	9
202	1.573	1.574	6
205	1.539	1.541	9
1,0,20	1.529	1.529	15
208	1.483	1.486	9
0,0,24	1.456	1.455	21
2,0,10	1.439	1.440	4
2,0,11	1.415	1.415	6
2,0,12	1.391	1.389	16
2,0,13	1.361	1.362	4

[a] Reflections allowed to run off scale to emphasize the weak peaks. [b] The (00*l*) reflections are relatively too strong because of some preferred orientation.

taken as 5.835, 5.90, 6.160, and 6.10 Å, respectively.

In the case of cobaltocene, we have estimated the dimensions as 6.60 Å for the ring diameter and 6.80 Å along the fivefold axis from the bond distances determined by X-ray diffraction and van der Waals radii. We note that Dines[7] gave a value of 5.60 Å for the ring diameter which we consider too small. Our estimates indicate that the molecule is nearly spherical so that the lattice expansion in this case gives no information about the orientation. However, in the case of (cobaltocene)tantalum disulfide wide-line NMR studies[18] supported Dines' conjecture that the fivefold axis of cobaltocene lay parallel to the layers. The proton resonances broaden at 245 K and again at 80 K; the changes in second moments at 245 K were fitted to a freezing out of the rotation of the C_5 axis in the plane parallel to the layers at 245 K and those at 80 K were fitted to the cessation of ring rotation about C_5.

All the lattice expansions observed are smaller than calculated on the basis of van der Waals radii. In part this may be due to some contraction of the molecule on cation formation, but the major proportion is more likely to be associated with compression under ionic packing forces. A number of significant variations in lattice expansions with changes in the organometallic compound are observed. For example, the series of compounds (Table I) where one ring is cyclopentadiene show an increase in expansion with increasing diameter of the other ring suggesting that all of these molecules adopt an orientation in which the principal molecular axis is parallel to the layers. The constancy of the expansions for the molybdenum arenes, however, suggests the alternative orientation with the planes of the carbocyclic rings parallel to the layers. It is significant that all compounds with one cyclopentadiene ring and no ring substitution have stoichiometries close to 0.25 whereas the arenes have lower compositions which decrease with increasing ring substitution.

A striking feature of the lattice expansions for the intercalates in Table III is the large increase in expansion for the 1,1′-diisopropylcobaltocene. This increase in expansion, 0.4–0.65 Å, compared with the case of the 1,1′-bis(dimethyl) and 1,1′-di-*n*-butyl compounds, which are closely similar, is observed in both TaS_2 and ZrS_2. A consistent explanation of this observation is an orientation of the organometallic molecule with the rings parallel to the layers. The methyl groups point away from and the H atoms point directly toward the sulfur layers. The effective van der Waals length of the molecule along the principal molecular axis is increased relative to those of the other substituted derivatives, which, if they were to adopt the same orientation, should have a smaller expansion. The rings parallel to the layers orientation proposed for the 1,1′-diisopropyl-substituted cobaltocene would be expected to give rise to a larger expansion than the orientation in which the principal molecular axis is parallel to the layers. However, we note that for (1,1′-dimethylcobaltocene)- and (1,1′-di-*n*-butylcobaltocene)zirconium disulfide the lattice expansions are identical with those of the intercalates of unsubstituted cobaltocene, 5.34, 5.34, and 5.35 Å. For the analogous TaS_2 compounds there is agreement between the values for the 1,1′-di-*n*-butyl derivative and cobaltocene, 5.53 and 5.47 Å, though the 1,1′-dimethyl value is somewhat larger (5.68 Å). As for the arene series the stoichiometries decrease with increasing ring substitution though the 1,1′-dimethyl compounds have compositions close to 0.25.

Clearly, both orientation and stoichiometry of organometallic intercalates depend subtly on the relative importance of guest–guest and guest–host interactions. The parallel orientations of the principal molecular axis favors π interactions between neighboring molecules as found in organic donor–acceptor complexes, and the perpendicular orientation favors a bonding interaction between the π-electron system of the rings and the sulfur layers. The failure to intercalate 1,1′-di-*tert*-butylcobaltocene either by direct means or by ion exchange may reflect a steric inhibition of both types of bonding interaction. Much larger expansions than expected for 1,1′-di-*tert*-butylcobaltocene are frequently observed for 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 $(\eta\text{-C}_6\text{H}_6)_2\text{Mo}$ and $(\eta\text{-C}_6\text{H}_6)_2\text{Cr}$ 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; $[(\eta^5\text{-MeC}_5\text{H}_4)_2\text{Co}]_{0.21}\text{TaS}_2$, 65353-19-7; $[(\eta^5\text{-}i\text{-PrC}_5\text{H}_4)_2\text{Co}]_{0.17}\text{TaS}_2$, 65254-96-8; $[(\eta^5\text{-}n\text{-BuC}_5\text{H}_4)_2\text{Co}]_{0.13}\text{TaS}_2$, 65254-97-9; $\{[(\eta^5\text{-MeC}_5\text{H}_4)_2\text{Co}]^+\text{I}^-\}_{0.14}\text{TaS}_2$, 65353-21-1; $\{[(\eta^5\text{-}i\text{-PrC}_5\text{H}_4)_2\text{Co}]^+\text{I}^-\}_{0.07}\text{TaS}_2$, 65254-99-1; $\{[(\eta^5\text{-}n\text{-BuC}_5\text{H}_4)_2\text{Co}]^+\text{I}^-\}_{0.05}\text{TaS}_2$, 65255-01-8; $\{[(\eta^6\text{-C}_6\text{H}_6)_2\text{Cr}]^+\text{I}^-\}_{0.13}\text{TaS}_2$, 65319-75-7; $\{[(\eta^6\text{-C}_6\text{H}_6)_2\text{Mo}]^+\text{I}^-\}_{0.15}\text{TaS}_2$, 65255-03-0; $\{[(\eta^5\text{-C}_5\text{H}_5)(\eta^6\text{-C}_6\text{H}_6)\text{Fe}]^+\text{PF}_6^-\}_{0.16}\text{TaS}_2$, 65255-04-1; $\{[(\eta^5\text{-C}_5\text{H}_5)_2\text{Co}]^+\text{I}^-\}_{0.20}\text{TaS}_2$, 67464-35-1; $[(\eta^5\text{-MeC}_5\text{H}_4)_2\text{Co}]_{0.25}\text{ZrS}_2$, 67464-36-2; $[(\eta^5\text{-}i\text{-PrC}_5\text{H}_4)_2\text{Co}]_{0.15}\text{ZrS}_2$, 67464-37-3; $[(\eta^5\text{-}n\text{-BuC}_5\text{H}_4)_2\text{Co}]_{0.13}\text{ZrS}_2$, 67464-38-4; $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Co}]_{0.25}\text{ZrSe}_2$, 67464-39-5; $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Co}]_{0.25}\text{VSe}_2$, 67464-40-8; $[(\eta^6\text{-C}_6\text{H}_6)_2\text{Mo}]_{0.16}\text{ZrS}_2$, 67464-25-9; $[(\eta^6\text{-C}_6\text{H}_6)_2\text{Cr}]_{0.16}\text{ZrS}_2$, 67464-26-0; $(\eta^5\text{-}t\text{-BuC}_5\text{H}_4)_2\text{Co}$, 59610-19-4; dimethylfulvene, 2175-91-9; $[(\eta^5\text{-}t\text{-BuC}_5\text{H}_4)_2\text{Co}]^+\text{PF}_6^-$, 67464-27-1; $[(\eta^5\text{-}i\text{-PrC}_5\text{H}_4)_2\text{Co}]^+\text{PF}_6^-$, 33635-72-2; $[(\eta^5\text{-}n\text{-BuC}_5\text{H}_4)_2\text{Co}]^+\text{PF}_6^-$, 67464-29-3; $[(\eta^6\text{-C}_6\text{H}_5\text{CH}_3)_2\text{Mo}]_{0.13}\text{ZrS}_2$, 61746-48-3; $[(\eta^6\text{-C}_6\text{H}_3(\text{CH}_3)_3)_2\text{Mo}]_{0.08}\text{ZrS}_2$, 61746-49-4; $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Cr}]_{0.25}\text{ZrS}_2$, 61746-51-8; $[(\eta^6\text{-C}_6\text{H}_6)(\eta^5\text{-C}_5\text{H}_5)\text{Cr}]_{0.24}\text{ZrS}_2$, 67464-30-6; $[(\eta^7\text{-C}_7\text{H}_2)(\eta^5\text{-C}_5\text{H}_5)\text{Cr}]_{0.25}\text{ZrS}_2$, 62343-38-8; $[(\eta^8\text{-C}_8\text{H}_8)(\eta^5\text{-C}_5\text{H}_5)\text{Ti}]_{0.23}\text{ZrS}_2$, 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: $\text{TX}_4 + 2\text{A}_2\text{S} \rightarrow \text{TS}_2 + 4\text{AX}$. 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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