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Tetrahydroborate Intercalation Reagents. Convenient, Straightforward Routes to Known and New Types of Layered Intercalation Compounds

Sir:

Current interest in the intercalation of ions and molecules into layered inorganic lattices derives from the importance of such processes/materials in high-density energy storage devices[1] (e.g., Li_xTiS_2, $Li_xV_3O_8$), heterogeneous catalysis[1a,2] (e.g., Co_xMoS_2, Ni_xWS_2 in HDS processes), and shape-selective adsorption/catalysis.[3,4] Solids prepared by intercalation reactions may also exhibit unusual physical properties such as enhanced electronic conductivity,[5] fast ion conductivity,[6] and even superconductivity.[7] Classes of host matrix materials that undergo intercalation include transition-metal oxides (e.g., MoO_3, V_2O_5, VO_2, WO_3), chalcogenides (e.g., TiS_2, TaS_2, $MoSe_2$, Mo_6S_8, $ZrSe_3$), and chalcogenohalides (e.g., FeOCl, VOCl), clay minerals, and others.

Traditional low-temperature approaches to intercalation compounds are frequently rather specific in applicability and inconvenient. Thus, organo alkali-metal reagents are extremely air- and moisture-sensitive, the approach appears limited to Li^+ insertion (eq 1),[8] and the reaction is not always clean.[9] Iodide

$$x\,n\text{-BuLi} + A \rightarrow (Li^+)_x(A^{x-}) + n\text{-octane} + n\text{-butane} + 1\text{-butene} \qquad (1)$$

reagents are somewhat more versatile (e.g., eq 2 and 3)[10,11] but

$$x\text{NaI} + \text{FeOCl} \xrightarrow{\text{ROH}} [\text{Na}_x(\text{ROH})_y]\text{FeOCl} + (x/2)\text{I}_2 \qquad (2)$$

$$x\text{LiI} + \text{V}_2\text{O}_5 \xrightarrow[\text{ROH}]{\text{CH}_3\text{CN}} \text{Li}_x\text{V}_2\text{O}_5 + (x/2)\text{I}_2 \qquad (3)$$

are not effective for metal chalcogenides and some oxides (MoO_3, WO_3), presumably due to the poor reducing power of iodide. Sodium dithionite is superior in this regard, and a wide variety of solids can be intercalated.[12] However, dithionites other than sodium are not readily available, and the solubility characteristics of $Na_2S_2O_4$ have so far restricted this approach to aqueous media, where the intercalation of aquated Na^+ results. Moisture-sensitive hosts[13] (e.g., early-transition-metal chalcogenides, FeOCl) are not amenable to this approach, unless the aquated products are desired. Finally, cation-exchange reactions can be used for some intercalation processes.[14]

In this report we present preliminary results concerning a more general method of conveniently intercalating a variety of cationic molecules into layered solid matrices using tetrahydroborate reagents. In this case, the BH_4^- anion acts as the reducing agent, and cation intercalation occurs with concomitant generation of gaseous B_2H_6 and H_2 (eq 4). In the majority of instances, this

$$x(\text{Cat}^+)\text{BH}_4^- + A \rightarrow (\text{Cat}^+)_x[A^{x-}] + (x/2)\text{B}_2\text{H}_6 + (x/2)\text{H}_2 \qquad (4)$$

reaction proceeds cleanly without undesirable byproducts.[15,16] Another advantage of this method is that it does not require water as solvent, and most tetrahydroborate reagents can be handled easily in the air. A variety of solvents can be used depending upon the characteristics of the particular tetrahydroborate salt. A great diversity of cations can be used, some of which are unusual and many of which are commercially available as tetrahydroborate salts: Li^+, Na^+, K^+, R_4N^+, transition-metal complexes,[17] etc. Host solids that can be intercalated span a wide range from transition-metal oxides to chalcogenohalides and dichalcogenides, viz. MoO_3, V_2O_5, FeOCl, TaS_2, and TiS_2.

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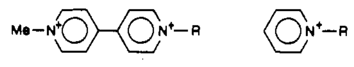

($R = C_{16}H_{33}$), using the iodide salts (Kanatzidis, M. G.; Marks, T. J., manuscript in preparation).

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Table I. Intercalated Products Obtained by Using BH_4^- Reagents

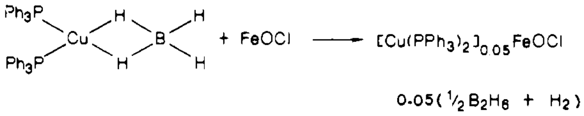
compd, $(Cat^+)_x[A^{x-}]$[a]	d,[b] Å	Δ,[c] Å	solvent	[A]:[BH_4^-] ratio	time[d]	temp, °C	color
$Li_{0.76}MoO_3$	8.28	1.35	ether	1:0.80	12 h	25	dark blue
$Na_{0.55}MoO_3$	8.79	1.86	*i*-PrOH	1:1	5 h	65	blue
$Na_{0.82}(H_2O)_{1.23}MoO_3$	9.76	2.83	wet EtOH	1:11	6 h	60	blue
$K_{0.41}MoO_3$	8.49	1.27	*i*-PrOH	1:1	12 h	65	blue
$(Me_4N)_{0.3}(MeOH)_{0.3}MoO_3$	11.94	5.01	DMF/MeOH	1:1	5 days	70	blue
$(Et_4N)_{0.3}MoO_3$	12.63	5.7	THF/Me_2SO	1:1	6 days	80	blue
$Li_{0.88}V_2O_5$	4.98	0.61	ether	1:1	4 h	25	dark green
$Li_{0.47}V_2O_5$	4.50	0.13	ether	1:1	3 h	25	dark green
$Li(H_2O)_3FeOCl$	11.33	3.35	wet ether	1:13	2 h	25	black
$Na_{0.6}(MeOH)_{0.3}FeOCl$	15.10	7.12	MeOH	1:1	2 h	25	black
$K_{0.26}FeOCl$	9.02	1.04	MeOH	1:0.9	2 h	25	black
$(Bu_4N)_{0.13}FeOCl$	15.78	7.80	CH_3CN	1:1	5 h	50	black
$[(Ph_3P)_2Cu]_{0.05}FeOCl$	16.245	8.26	$CHCl_3$	1:0.25	6–8 h	55	black
$Li_{0.08}TaS_2$	6.241	0.261	pyridine	1:1.9	6 h	65	metallic gray
$Li_{0.21}TaS_2$	6.280	0.300	pyridine	1:5	10 h	65	metallic gray
$Li_{0.17}(H_2O)_{0.4}TaS_2$	7.53	1.55	wet MeOH	1:3.5	12 h	25	metallic gray
$Na_{0.40}TaS_2$	7.284[e]	1.304	pyridine	1:1.4	22 h	65	metallic gray
$Na_{0.4}(H_2O)_4TaS_2$	11.94	5.96	wet pyridine	1:1.4	22 h	65	metallic gray
Li_xTiS_2	6.12	0.41	EtOH	1:1	22 h	65	metallic gray

[a] Only some values of x are shown. A wide range in x is achievable depending on the [A]:(Cat)BH_4 ratio and reaction times. [b] Interlayer separation. [c] Expansion in interlayer separation from unintercalated solid. [d] Reaction time; strongly dependent on particle size. The solids were finely ground in a mortar and pestle. [e] Products contaminated with $(py)_xTaS_2$ and possibly $Na_x(py)_yTaS_2$ phases; total Na:Ta ratio 0.4.

In a typical reaction, the BH_4^- salt is dissolved in an appropriate solvent (THF, ROH, pyridine) in which the host solid is suspended. Depending on the solid and cation used, vigorous or slow gas evolution occurs[15] followed by a color change of the solid. As judged by X-ray diffraction (disappearance of starting material), the reaction is usually complete within several hours at room temperature or slightly above. In the case of alkali-metal ions, the reaction is carried out under anhydrous conditions to avoid formation of an H_2O-solvated phase. Li^+, Na^+, and occasionally K^+ intercalates are particularly hygroscopic and form $M_x(H_2O)_x[A^{x-}]$ phases. If the latter phases are desired, then controlled amounts of water are added to the reaction medium.

The intercalation products were characterized by infrared spectroscopy, elemental analysis, and X-ray powder diffraction. Relevant data are compiled in Table I. Stoichiometries obtained are representative results for particular A:BH_4^- ratios and the reaction conditions stated. They do not necessarily represent maximum possible degrees of reduction. The reported increases in interlayer separation upon intercalation are a measure of the size of the inserted ions and accompanying coordination spheres.

We find that the FeOCl matrix is the most susceptible to intercalation using the BH_4^- method. For instance, the large Bu_4N^+ cation enters FeOCl in a few hours. The ease with which the FeOCl lattice can be intercalated is also demonstrated by the introduction of the large cationic transition-metal complex $(Ph_3P)_2Cu^+$ in the remarkable reaction



(5)

A substantial interlayer expansion of 8.32 Å is associated with this intercalation. The full structural and physical characterization of this compound is in progress.

Alkai-metal ions appear to undergo insertion most readily in all of the solids examined. Generally, K^+ intercalates more slowly into MoO_3 and V_2O_5 than does Na^+ or Li^+. The last ion undergoes insertion into TaS_2 and TiS_2 much more readily than does sodium, as expected[5,13,18] from its greater ion mobility. Although various more specific procedures have previously been employed to intercalate tetraalkylammonium ions into given host lattices,[19–21] the present tetrahydroborate approach appears to be the most general to date (e.g., it is effective with MoO_3). Interestingly, tetraalkylammonium salts and $Cu(PPh_3)_2^+$ do not undergo intercalation into metal dichalcogenides under typical reaction conditions. Furthermore, none of the tetrahydroborate reagents show any reactivity toward graphite. It is obvious from the observations presented here and from the redox intercalation literature[3] that whether a particular cation will enter the lattice of a host material is dictated by a complex combination of thermodynamic and kinetic factors.

Tetrahydroborate reagents provide an alternative and convenient route to a wide range of intercalation materials. A significant advantage of these reagents is broad scope and commercial availability. Depending on the host material, a diversity of cations can be intercalated, some of them not readily inserted by other means. Thermodynamically, the method is limited by the reducing ability of BH_4^-. Its reducing ability is greater than that of I^- but less than that of n-Bu^-. In addition, we have demonstrated that it is possible to obtain novel intercalation compounds not available by other methods, i.e., $[(Ph_3P)_2Cu]_{0.05}FeOCl$. Work along those lines is continuing in our laboratory.

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Department of Chemistry and Materials
Research Center
Northwestern University
Evanston, Illinois 60201

M. G. Kanatzidis
T. J. Marks*

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