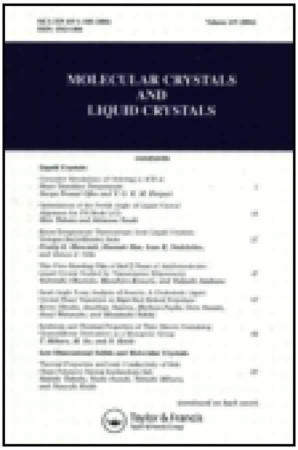

## Molecular Crystals and Liquid Crystals

# New Information On 2H-$TaS_2$ Intercalation Chemistry With Organic Bases

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# NEW INFORMATION ON 2H-$TaS_2$ INTERCALATION CHEMISTRY WITH ORGANIC BASES

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Abstract This contribution describes a quantitative chemical study of the 2H-$TaS_2$ + pyridine reaction at 115°C under rigorously anaerobic and anhydrous conditions (as well as with added water and other reagents). Small amounts of pyridine coupling products (primarily 4,4'-bipyridine) are observed which increase then fall off with increasing water concentrations. Based upon a number of mechanistic tests, the coupling chemistry is tentatively associated with the formation of pyridine cation radicals. 2H-$TaSe_2$ effects the same chemistry without intercalation.

The intercalation of organic bases and other electron donors into the van der Waals gaps of layered transition metal dichalcogenides results in significant changes in structural and electronic properties.[1] For organic intercalants, surprisingly little is understood about the actual intercalation process (i.e., is redox chemistry involved?) despite an extensive literature and the criticality of such chemistry to many applications[2] (e.g., electrode/electrolyte compatibility in advanced batteries). In order to better define the nature of metal chalcogenide/organic molecule interactions, we have initiated a study of the model system 2H-$TaS_2$ + pyridine under rigorously controlled conditions.

All operations were carried out on a preparative high vacuum line using flamed glassware and rigorously purified inert gases, or in a glove box with a high capacity atmosphere recirculating system. 2H-$TaS_2$ was prepared by a modification of the Revelli procedure[3] and was characterized by elemental analysis and X-ray powder diffraction. Pyridine was dried (<35 ppm $H_2O$) by refluxing over BaO followed by repeated vacuum transfers onto freshly activated 3A molecular sieves. Products were analyzed by GC, GC/MS, pyrolysis MS, elemental analysis, X-ray diffractometry, and Toepler pump measurements.

The first objective was to investigate the facility, reaction conditions, and reaction mechanism(s) associated with the (controversial)[4,5] observation that pyridine intercalation is accompanied by the formation of large quantities of the coupling products 4,4'-bipyridine (**A**), 4,4'-thiobipyridine (**B**), and 4,4'-dithiobipyridine (**C**). Although 2H-TaS$_2$ behaves chemically as an oxidizing agent, **A**-**C** are not classical pyridine oxidation products.[6]

Intercalation reactions were conducted under scrupulously anaerobic and anhydrous conditions, as well as with measured amounts of added water (or other reagents). A Soxhlet reaction apparatus shown in Figure 1 allows constant extraction of products from the reaction zone by flowing pyridine. The pyridine solution can be studied as a function of time by sampling through the lower Kontes valve. It is thus possible to monitor the temporal aspects of product formation and to determine when reaction is complete.

A number of observations are general for reactions carried out at 115°C under a variety of conditions. First, although small amounts of **A** and far lesser amounts of **B** and **C** are observed, and the quantities are somewhat dependent upon water present (*vide infra*), total yields of coupling products are *never* greater than a 0.03 molecule/Ta atom. Pyrolysis mass spectrometry indicates that, for reactions carried to completion in the extractor, negligible amounts of **A**-**C** remain intercalated. Toepler measurements reveal that detectable quantities of gaseous H$_2$S or H$_2$ are not evolved during the reaction. We also find that neither added **B**, **C**, nor 4-hydroxypyridine have any detectable effect on the coupling chemistry. Monitoring product formation as a function of time reveals that **A**, **B**, and **C** are formed simultaneously, with no evidence that one species is the precursor of the others. Addition of

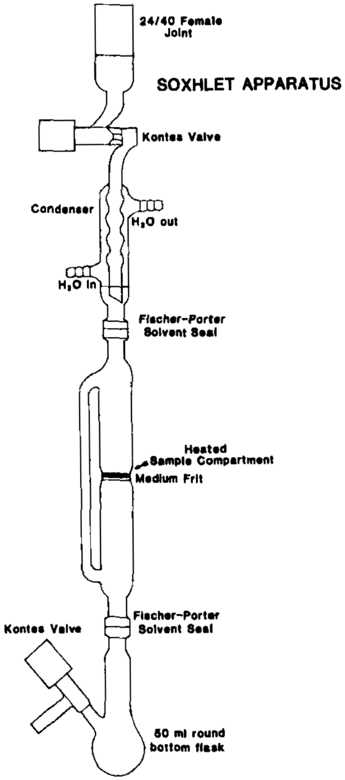

FIGURE 1 Soxhlet extraction apparatus for 2H-TaS$_2$ intercalation reactions

benzene and toluene to the reaction solutions does not result in cross-coupling products nor have free radical species been detected by EPR spin traps. Interestingly, 2H-TaSe$_2$ also yields $\underset{\sim}{A}$ but *does not* undergo intercalation.

The effect of added water on the intercalation process is complicated, and experiments are still in progress. However, the data in Table I indicate that coupling is low under very anhydrous conditions, increases with increasing water content, and then is quenched by large quantities of water. Interestingly, negligible water is consumed in the reactions.

TABLE I Coupling Product Yields for 2H-$TaS_2$ + Pyridine as a Function of Added Water[a]

| $TaS_2$ (μmol) | Pyridine (mmol) | Coupling products[b] (μmol) | $H_2O$ Before (μmol) | $H_2O$ After[c] (μmol) |
|---|---|---|---|---|
| 4160 | 303 | 68 | 45 | d |
| 4160 | 346 | 122 | 85 | 77 |
| 3250 | 345 | 116 | 254 | d |
| 4060 | 348 | 23 | 656 | 708 |
| 3950 | 320 | 24 | 605 | d |

[a] Reaction at 115° until product yield constant (3-5 days).
[b] Predominantly 4,4'-bipyridine.
[c] After completion of reaction.
[d] Not measured.

More information will be required for a complete mechanistic picture of the 2H-$TaS_2$ + pyridine intercalation/coupling chemistry. However, obvious analogies to the oxidative (radical cation) oligomerization of pyrrole, thiophene, and benzene are apparent. It is moreover conceivable that the structure of the layered chalcogenide significantly effects both the chemo- and regioselectivity of transformations involving pyridine radical cations.

## ACKNOWLEDGMENTS

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