

as that presented by the isocyanides occurs, exceptional bonding results.

The high stability of these products is attested by their TGA behavior, which exhibits temperatures for 50% loss of the guest at greater than about 250 °C above their normal boiling points. This value can be compared with that for the amine intercalates, which lose half of their guests within 50–150 °C of their normal boiling points. These values represent a rough measure of stability of the complexes.

It can be surmised from the observed *c*-axis expansions of the methyl isocyanide and butyl isocyanide products that the more likely configuration of the guest positions is parallel to the layers of TiS_2 and TaS_2 (alternative II in Figure 1). Such a structure is consistent with a stoichiometry of 0.5 guest/host unit for the methyl isocyanide products, but for butyl isocyanide a more likely ratio is 1:3. This is not in accord with the experimental uptake and once again suggests the difficulty in isolating a pure product. In the case of benzyl isocyanide, the observed expansion of 12.3 Å can be explained by either alternative structure, as long as it is bilayered.

Another indicator of the disparate bonding behavior of the isocyanide– TaS_2 compounds is the relatively large enhancements measured in the superconducting transition behavior. Intercalation has been found to perturb the Fermi level electrons of TaS_2 so as to cause an increase in the superconducting transition temperature from an initial value of 0.8 K (for the 2H polymorph) to values in the range 2.0–5.3 K.^{2,10} There have been attempts to correlate the donation of charge to the host with this effect,^{3,11} but the results remain questionable. What can be said is that whatever the controlling factors, the isocyanides induce the greatest increment thus far found, the range being 5.2–5.8 K.

Anomalous electronic effects were also exhibited by the TiS_2 complex of methyl isocyanide in its thermoelectric coefficient. Most previous neutral guests, such as ammonia, lead to compounds having Seebeck coefficients on the order of 150 $\mu\text{V}/\text{K}$.¹² However, for TiS_2 -methyl isocyanide the value is 40 $\mu\text{V}/\text{K}$.

In order to test the emerging proposition that back-bonding to intercalated guests can be a significant component in the formation of intercalation compounds with the layered dichalcogenides, a simple trial was undertaken. The behavior of triethylamine and triethylphosphine in contact with TaS_2 at 75 °C was compared. Although of comparable basicity ($\text{p}K_a$ of triethylamine is 11;¹³ for triethylphosphine the value is 8.7⁸), the phosphine has vacant d orbitals which allow for back-acceptance of electron density. After 3 days, the phosphine had substantially incorporated into the host (verified by x-ray diffraction) whereas the amine had not. It should, of course, be borne in mind that comparing rates of reaction does not directly relate to relative bond strengths (in fact, the inverse may be true in some cases). But this example serves to illustrate that the effect of π acidity can influence kinetics (nucleation and diffusion processes) as well as equilibrium electronics, when other factors, such as geometry and basicity, are about equivalent and the complicating factors of hydrogen bonding¹⁴ are eliminated. Interestingly, the triethylphosphine intercalation complex of TaS_2 , having an interlayer dilation of 4.0 Å, does not deintercalate even at 400 °C and therefore represents an exceedingly stable molecular complex.

Conclusions

Whereas previous workers have attempted to correlate the basic (donor) character of guests with the parameters of intercalation in the transition metal dichalcogenides, it is clear that other factors must now be also considered.¹⁵ Nitriles and isocyanides both have $\text{p}K_a$ values well within the regime of those weak Lewis bases which do not intercalate; however, not only do the latter intercalate but they also form remarkably

stable compounds as assessed by their thermogravimetric behavior. In addition, the products have anomalously large perturbing effects on the Fermi electrons of both Ti - and TaS_2 , as seen in the thermoelectric coefficient and superconducting transition temperatures, respectively. It is reasonable to implicate the well-known superior back-bonding power of the isocyanides in these phenomena, especially when bearing in mind the electron-rich nature of the ions directly encountered by the incorporated guest, the chalcogenides.

Acknowledgment. The author wishes to express his gratitude to A. H. Thompson, who determined the superconducting transition temperatures for the TaS complexes, and to L. B. Ebert for running the thermoelectric experiment on the TiS_2 -methyl isocyanide product. In addition, he appreciates the able assistance of J. Picone, S. Pagnucco, and B. Castellano.

Registry No. $\text{TaS}_2(\text{CH}_3\text{NC})_x$, 65059-28-1; $\text{TiS}_2(\text{CH}_3\text{NC})_x$, 65059-29-2; $\text{TaS}_2(\text{C}_4\text{H}_9\text{NC})_x$, 65059-30-5; $\text{TaS}_2(\text{C}_6\text{H}_5\text{CH}_2\text{NC})_x$, 65059-31-6.

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- (15) It has been pointed out by a referee that the present discussion does not take into account the very recent evidence presented by Schöllhorn (R. Schöllhorn and H. D. Zagefka, *Angew. Chem.*, **89**, 193 (1977)) that molecular intercalation into layered transition metal dichalcogenides proceeds with some degree of ionization. It is implied that covalent overlap between guest and host is of little relevant consequence. However, in those cases (such as presented here) where no obvious direct correlation between ionization potential of a molecule and its tendency to incorporate exists, the effects of covalency seem pertinent.

Contribution from Exxon Research and Engineering Company, Linden, New Jersey 07036

A "Melting" Phase Transition in Tantalum Disulfide-Octadecylamine Intercalates¹

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The structure and dynamics of intercalated linear alkyl compounds present an attractive model for lipid membranes and other reduced dimensional phase phenomena, and in this regard particular attention has been paid to the clay host materials.³ Interesting effects have been seen in other lamellar matrices; for instance, the apparent melting transition of a series of *n*-alkylamines incorporated within the layers of nickel cyanide has recently been described⁴ and elaborated upon.⁵ In that system, the chains are inclined about 50° relative to the basal surface of the host. A distinct hiatus was observed in the otherwise monotonic increase in layer-layer separation

as a function of chain length. This discontinuity occurs at about ten carbons, and the authors attribute it to the point below which the guests are melted within the solid at room temperature.⁴ *n*-Decylamine itself melts at about 10 °C below room temperature; thus the ordering effect imposed by the planar host on the guest is evident.

In the case of the layered MPS_3 hosts ($M = Mg, Zn,$ and Mn) Yamanaka posits both a parallel and a pseudo-perpendicular structure for alkylamine intercalates having carbon numbers three to eight.⁶

For the lamellar transition metal dichalcogenides, it was found that below carbon number ten, intercalated *n*-alkylamines adopt a parallel orientation relative to the host layers, but for longer chains, they form perpendicular bilayers.⁷ It is likely that this phenomenon derives in part also from the effective melting point of the intercalated guest phase, once again falling at room temperature for carbon number around ten. The explanation given, that parallel oriented guests take up increasing basal area per site, is not to be ignored.

Another dramatic manifestation of the delicate balance of the energetics of intercalated phases is the phenomenon of staging. Commonly, on driving off half of the guest in a fully loaded compound (or on contacting the starting host with just half of the guest required for full occupation) second-stage structures are afforded in which every other interlayer is voided. For the transition metal dichalcogenide intercalates, the remaining occupied interlayers seem to retain the structure of their first-stage counterparts, as is the case with stearamide.⁷

Whenever any given intercalation compound (such as those with which we are dealing here) is forced to relinquish half of its guest molecules, it has three alternative modes: (a) it may form a second-stage product; (b) a first stage structure may be maintained with half of the initial sites unoccupied; or (c) two phases can result, the starting fully occupied compound and vacated host.

In our ongoing investigation of the behavior of the molecular intercalation compounds of the layered dichalcogenides, we have recently found that with *n*-octadecylamine the first example of the second mode above is exhibited—namely, that a distinct phase first-stage compound is afforded on half deintercalation of the fully loaded (2/3 guest to host) product. Furthermore, we have followed quantitatively the differential scanning calorimetric behavior of both the 1/3 and 2/3 complexes and studied their melting behavior.

Experimental Section

n-Octadecylamine was found to be suitable for use as received from Aldrich Chemicals, but precaution must be taken to open and handle the material only in an inert atmosphere, since it quickly reacts with ambient carbon dioxide. The amine melts completely at 54 °C, but contamination with CO_2 yields a higher melting impurity. The host, $2H-TaS_2$, was prepared from the elements as described.⁸

Thermogravimetry and differential scanning calorimetry were run on a Du Pont 900 series instrument. X-ray diffraction patterns on Mylar covered powders were run using $Cu K\alpha$ radiation on a Philips diffractometer.

Intercalation reactions were run in sealed Pyrex tubes which were loaded and opened in a drybox with a helium atmosphere. The saturated product, $TaS_2(C_{18}H_{37}NH_2)_{2/3}$, is afforded by contacting the starting host with excessive amine for several days at 100 °C. Elemental analyses and TGA both verify the stoichiometry.

The half-saturated product, $TaS_2(C_{18}H_{37}NH_2)_{1/3}$, is isolated as a pure single phase after heating a quantity of the starting host with exactly one-third a molar equivalent of the guest at about 150 °C for 4 days. Again, the stoichiometry was corroborated by analyses and TGA. It is crucial to be sure about the stoichiometry, since Mathey et al.⁹ have shown that for the case of nickel cyanide-alkylamines, excessive guest can be incorporated within the saturated products to considerable extents.

Both products exhibited the same superconducting transition temperature, 3 K, when measured on a vibrating magnetometer (performed by A. H. Thompson).

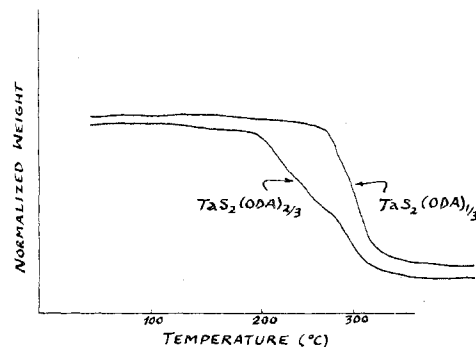


Figure 1. Thermogravimetry of the two *n*-octadecylamine (ODA) complexes of TaS_2 . Note that weight loss is normalized.

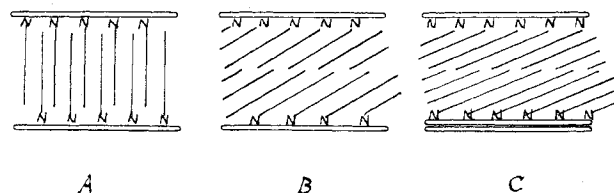


Figure 2. Three alternative structures for the 1/3 complex: A, first-stage perpendicular monolayer; B, first-stage bilayer with 34° skewing of chains; C second-stage bilayer with 26° skew.

Attempts to measure changes in the d spacings on passing through the phase transition using a variable-temperature goniometer yielded ambiguous results.

Results and Discussion

The thermogravimetric behavior of the 2/3 (fully loaded) product suggests that in the deintercalation process there are two somewhat differing binding sites (Figure 1). The first of these dissociates at about 200 °C (heating rate 10 °C), the second at about 300 °C. That the latter likely corresponds to the prepared 1/3 product is evidenced by comparison with its observed weight loss at 300 °C in one step. As reported previously^{7,10} the observed basal repeat distance as seen in its x-ray powder diffraction pattern proves that the structure of the 2/3 complex involves the perpendicularly oriented bilayered configuration with approximately 50 Å between the TaS_2 slabs—double the length of a guest molecule. The repeat distance found for the 1/3 complex, however, was determined to be 34 Å from x-ray diffraction measurements, leaving about 28 Å between the layers for the guests. Were the 1/3 product a typical second-staged bilayered structure, the repeat distance would be 62 Å (the dimension of the first stage complex plus 6 Å for the additional slab of TaS_2). Such in fact is the case for stearamide, which differs from octadecylamine in having a terminal $-C(=O)NH_2$ group instead of $-CH_2NH_2$. If one assumes a perpendicular orientation for the 1/3 product, the interlayer dilation is about 3 Å greater than the chain length. (If a bilayered structure is assumed, an angle of inclination of about 34° would be needed to yield the observed repeat distance, but this alternative does not explain the stoichiometry; an even less likely possibility is a bilayered second-stage structure having the chains inclined 26° to the layers (see Figure 2).¹¹ Furthermore, second-stage products usually exhibit a reflection, or enhanced intensity, at the 2θ value corresponding to the voided layer-layer distance which in the present case would be 14.7°; however, this was not seen.) In view of these considerations, the most likely structure for the 1/3 complex is one having interleaved chains oriented upright on the layers, occupying just half of the sites of the 2/3 complex, and having the chain termini ($-CH_3$ groups) falling short of the opposing layers by about 3 Å (Figure 2).

The obvious question posed by these observations is: why do stearamide and octadecylamine follow such different routes

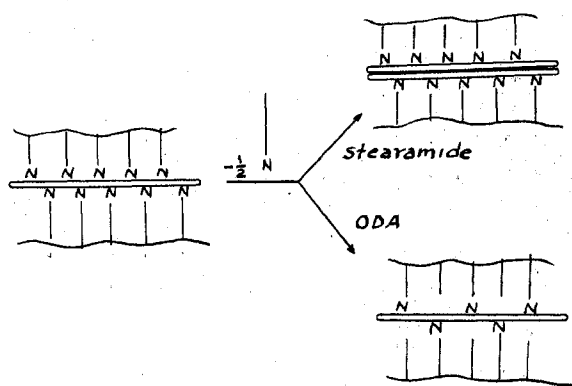


Figure 3. Two different courses followed by half evacuation of long chain guest complexes.

of partial deintercalation? In either $1/3$ complex the density of the guest phase, and hence of the guest-guest interaction, is about the same. The essential difference between them is the presence of layer-layer bonding and all guest-host bonding on one surface for the amide, as compared with having the same number of guest-host bonds distributed on both sides of each sheet in the case of the amine (see Figure 3). The amine, being a stronger Lewis base, likely interacts more strongly with the layer, and this may be why regaining layer-layer bonding at the expense of losing opposing guest-host bonds does not occur.

A test of the assumption of the insignificance of guest-guest bonding differences between the $2/3$ and $1/3$ octadecylamine complexes of TaS_2 is the evaluation of the heat of melting of the two guest phases. This was accomplished using differential scanning calorimetry (DSC) on the two complexes at temperatures far below any observed weight loss. Both complexes undergo a reversible phase transition at about $10-15^\circ C$ above the normal fusion point of the free guest, in keeping with the previous observation⁴ that intercalation modestly raises the melting transition temperature. *n*-Octadecylamine was first run to ascertain the accuracy of the method and yielded a value for its heat of fusion of 16.0 ± 1.5 kcal/mol. No literature comparison could be found, but an estimate using the group method was made by adding to the heat of fusion of octadecane (14.8 kcal/mol)¹² the difference in heats of fusion between methylamine and methane (1.24 kcal/mol).¹² In good agreement with the experiment, 16.0 kcal/mol is the resulting value.

The melting transition observed for the $1/3$ octadecylamine- TaS_2 complex was very similar in shape, and occurred at about $7^\circ C$ higher (Figure 4). The heat of the transition amounted to 5.2 kcal/mol (of amine). Conceptually, this means that about one-third of the freedom of the liquid phase is realized in the transition. On cooling and reheating, the DSC curve is very closely repeated. As shown in the figure, the curve for the $2/3$ complex was not as simple. The transition fell about $8^\circ C$ higher than the lower complex and exhibited additional structure. The measured enthalpy for all of the area amounts to 6.9 kcal/mol (of amine). However, reducing the area by ignoring the shoulder seen at $90^\circ C$ leads to the value 5.1 kcal/mol, in agreement with that of the $1/3$ complex. On cooling and passing through the transition again, the area of the shoulder relative to the main transition increased. So with this reservation in mind, it can be concluded that the intermolecular bonding in the two complexes is very nearly equal.

A different perspective of this transition has been seen in the broad-line NMR (performed by B. G. Silbernagel). For both complexes, the proton signal at room temperature was about 6.5 G in breadth, as expected for crystalline packing. However, on raising the temperature to $75-80^\circ C$, the lines

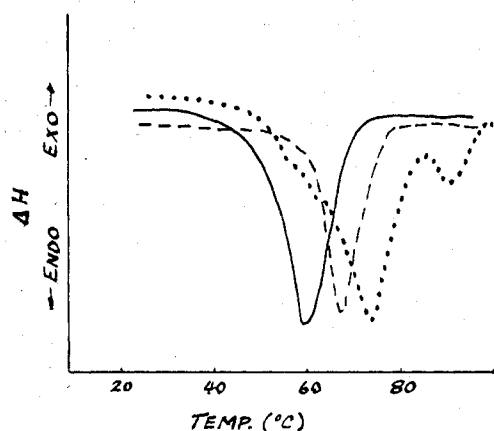


Figure 4. Differential scanning calorimetry results: solid line is *n*-octadecylamine, dashed line is the $1/3$ TaS_2 complex, dotted line is the $2/3$ complex. The scales are not the same. Data are in the text.

are essentially completely narrowed, indicating liquid-like motion.

It has and will continue to be demonstrated that by studying the behavior of bulk lamellar intercalated phases as models for lipid structures or surface films, insights into the structure and dynamics can be relatively more easily gained, and the valuable function as a model is thus served.

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Triplet-Singlet Emission of $Fe(CN)_5CO_3^{3-}$

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Excitation of a series of compounds containing Fe^{3+} with UV radiation gave in each case a broad structureless d-d luminescence band in the red¹ and near-infrared² regions. However, there are no known examples of emission from complexes of Fe^{2+} . It has been suggested that the absence of