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Linden, New Jersey 07036

Isocyanide Intercalation Complexes of Titanium and Tantalum Disulfide

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Received August 3, 1977

The lamellar transition metal dichalcogenides have been found to act generically as hosts for the intercalation of basic organics such as amines and hydrazines.[2,3] This behavior implies that the host materials possess Lewis acid character, which is consistent with the highly electronegative nature of these solids that, for instance, renders TiS_2 a promising cathodic component in a high energy density battery.[4] Relatively weak electron donors, such as alcohols or nitriles, cannot under reasonable conditions be forced to incorporate. However, although they are only marginally more basic than their isomers, isocyanides are found to form quite stable intercalates in several cases we now report. They thus constitute a significant new class of inclusion compounds for the layered dichalcogenides in that back-bonding to the donor is likely involved in the complexation interaction, and a rare insight into the guest–host bonding of such complexes is afforded.

Experimental Section

The layered host materials TiS_2 and 2H–TaS_2 used in this study were prepared in these laboratories by high-temperature contacting of the elements.[5] Methyl isocyanide was prepared according to the method of Schuster,[6] and the butyl and benzyl analogues were obtained from the Aldrich Chemical Co.

All preparative and workup procedures were conducted in a glovebox under helium. The reactions were run in sealed Pyrex tubes using 0.5–1.0 g of the solid host with excessive isocyanide (ca. 1–2 mL). After 4 days in an oven maintained at 100–150 °C (see Table I), the tubes were opened and the product was filtered and washed with dichloromethane and then dried. The products were analyzed for C–H–N, x-ray diffraction patterns were determined under a Mylar film on a Philips diffractometer with Cu Kα radiation, and thermogravimetry was performed on a Du Pont 900 series instrument. Superconducting transition temperatures were determined with a vibrating magnetometer.

The assignment of the stoichiometries of complex formation was complicated by the apparent formation of some intractable coproducts (which gave no powder patterns) leading to excessive weight gains and somewhat high C–H–N values. However, the TGA results, as given in the table summarizing the results, suggest 2:1 ratios (host to guest). That intercalation does occur is indicated by the powder diffraction patterns, and in Table II are listed the reflections for one of the compounds, the TaS_2–methyl isocyanide adduct.

To show that the product of deintercalation was nonisomerized isocyanide, approximately 300 mg of the butyl isocyanide intercalate of TaS_2 was heated in a flow of dry nitrogen to about 300 °C and the volatile product collected on a cold finger. Infrared spectroscopic examination of this oil revealed a band falling at 2160 cm^{-1}, indicating the presence of unchanged starting material. Nitriles have their stretching band at 2250 cm^{-1} [7], which was not observed. It should be noted that this experiment only proves that the isocyanide functionality remains intact; that it is unchanged butyl isocyanide is implied by its volatility.

Results and Discussion

In their complexation with most transition metal ions, isocyanides contrast markedly with nitriles. Possessing superior back-bonding abilities as a result of more effective π-accepting antibonding orbitals, they tend to interact strongly with softer, more electron-rich species.[8] It is therefore not difficult to conceive how and why such a factor might be a significant component in intercalative complexation with the layered dichalcogenides, although this effect has not previously been appreciated.

Table I. Summary of Experimental Results–$MS_2(RNC)_x$ Products[a]

M	R	Reaction temp, °C	x (based on TGA)	c-axis exptl, Å	T_c, K	$T_{D/2}$,[b] °C
Ta	CH_3	100	0.43	3.7	5.8	375
Ti	CH_3	150	0.53	3.7	c	325
Ta	C_4H_9	150	0.86	4.25	5.2	300
Ti	C_4H_9	150	(No reaction)			
Ta	$CH_2C_6H_5$	125	0.42	12.3	c	275

[a] All reactions were run for 4 days. [b] Temperature at which half of deintercalation occurs (from TGA). [c] Did not become superconducting above 1.5 K.

Table II. X-Ray Diffraction Data for TaS_2–Methyl Isocyanide Complex[a]

hkl	2θ, deg	d spacing, Å	Intensity[b]
001	9.08	9.73	s
002	18.28	4.85	s
003	27.42	3.25	m
100	31.30	2.86	w, br
102	36.24	2.48	w, br
004	37.00	2.43	m
103	41.90	2.15	w, br
005	46.70	1.94	m
110	55.16	1.66	w
111	56.08	1.64	w
006	56.78	1.62	m

[a] Hexagonal unit cell, $a = 3.32$, $c = 9.73$ Å. [b] Key: s, strong; m, medium; w, weak; br, broad.

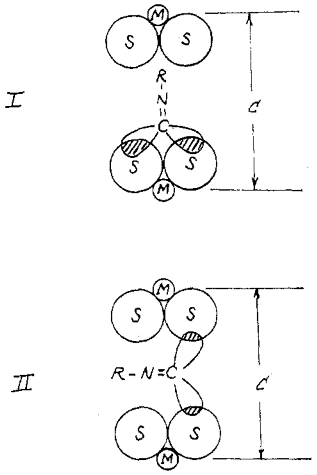

Figure 1. Perpendicular (I) and parallel (II) configurational alternatives for the structure of the isocyanide intercalation complexes. The π-accepting antibonding orbital on carbon is shown.

Since for all of the layered dichalcogenides the first coordination sphere of the metal ion is filled by six anions,[9] no direct bonding between an intercalated ligand and the metal is possible, and bonding must be mediated by the chalcogenides, which are rich in electron density. It is from these atoms that one could expect a back-flow of charge into an effective π acceptor which is situated between the host layers. The orientation of such a complex could either be perpendicular (plugged-in) to the layers, or the guests might be parallel, allowing for the possibility of interaction with both lamella (see Figure 1).

Naturally, the importance of the normal forward flow of electron density from the guest to the host is not to be discounted, in light of the considerable accumulation of observations with amines[2,3] (which are good σ donors, but poor π acceptors), as well as the fact that such excellent π acids (and poor donors) as carbon monoxide and trifluorophosphine do not intercalate. It appears that when an optimal situation such 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 it 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 μV/K.[12] However, for TiS_2–methyl isocyanide the value is 40 μV/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 (pK_a of triethylamine is 11;[13] for triethylphosphine the value is 8.7[8]), 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 bonding[14] 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 pK_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. Castellanto.

Registry No. $TaS_2(CH_3NC)_x$, 65059-28-1; $TiS_2(CH_3NC)_x$, 65059-29-2; $TaS_2(C_4H_9NC)_x$, 65059-30-5; $TaS_2(C_6H_5CH_2NC)_x$, 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.

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A "Melting" Phase Transition in Tantalum Disulfide–Octadecylamine Intercalates[1]

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Received August 8, 1977

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 described[4] 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

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