CHEMISTRY of MATERIALS

VOLUME 5, NUMBER 10 OCTOBER 1993

Communications

Unique Ammonia Reorientation in Sodium–Ammonia Intercalation Compounds of Titanium Disulfide

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Received July 10, 1992
Revised Manuscript Received March 8, 1993

Intercalation compounds of lamellar transition metal disulfides (TS_2) have been widely used to investigate properties of materials confined to two dimensions.[1–3] Solvated-cation intercalation compounds offer an excellent opportunity to study two-dimensional solvation chemistry by probing the relative strengths of their guest–host and guest–guest interactions. The two simplest solvents suitable for study of model solvated compounds are NH_3 and water.

Hydrated metal–TiS_2 intercalates exist in both monolayer and bilayer forms, whereas only monolayer compounds have been observed for NH_3-solvated systems.[3–5] This can be attributed to the greater cation solvation energy of aqueous intercalates. Unfortunately, no complete structural refinements for hydrated intercalates are currently available. However, the structure of $(ND_4^+)_{0.22}(ND_3)_{0.34}TiS_2^{0.22-}$ has recently been solved by Rietveld refinement of time-of-flight neutron powder diffraction (NPD) data, which provides the first detailed structural evidence from which solvated intercalate guest–guest and guest–host interactions can be assessed.[6] The ND_3 and ND_4^+ nitrogen positions are located at the center of trigonal prismatic guest sites, with both species distributed randomly over these sites. The ND_3 solvent adopts a planar structure, with two deuterium atoms hydrogen bonded to sulfur atoms in adjacent host-layers and the third located on the interlayer midplane. This structure is consistent with previous single-crystal proton NMR data, which indicate the C_3 axis of NH_3 is parallel to the host layers in nominally $(NH_3)_{1.0}TaS_2$.[7,8] Also, it has recently been proposed that the guest species associated with these ammonia intercalates may be better described as individual N and H atoms occupying specific crystallographic guest sites, rather than molecular and molecular-ion intercalants.[9]

The unique structures and guest–guest and guest–host interactions associated with several ammoniated metal–cation intercalates have been investigated recently.[5,10] Structural refinement of NPD data for $Li^+_{0.22}(ND_3)_{0.63}TiS_2^{0.22-}$ supports the presence of lithium–NH_3 complexes, $Li^+(ND_3)_3$.[10] Other ammoniated metal-cation ($M^{n+} = Ca^{2+}, Sr^{2+}, Ba^{2+}$, and Yb^{3+}) intercalates of TiS_2 also apparently contain discrete complexes having coordination numbers of 2, 3, or 6, depending on the nature of the metal and its concentration.[5] Herein, we describe the structural investigation of the sodium NH_3–TiS_2 intercalation system, which provides the first evidence for compositionally induced molecular reorientation in monolayer intercalation compounds.

Highly stoichiometric $TiS_2(Ti_{1.002}S_2)$ was used as the host material.[11,12] Both the host and intercalates were prepared, handled and investigated under rigorous inert-

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(1) Levy, F., Ed. *Intercalated Layered Materials*; D. Reidel: Dordrecht: Holland, 1979.

(2) Whittingham, M. S., Jacobson, A. J., Eds. *Intercalation Chemistry*; Academic Press: New York, 1982.

(3) Atwood, J. L., Davies, J. E. D., MacNicol, D. D., Eds. *Inclusion Compounds*; Academic Press: London, 1984.

(4) Lerf, A.; Schöllhorn, R. *Inorg. Chem.* **1977**, *16*, 2950.

(5) Ong, E. O.; McKelvy, M. J.; Dotson, L. A.; Glaunsinger, W. S. *Chem. Mater.* **1991**, *3*, 17.

(6) Young, Jr., V. G.; McKelvy, M. J.; Glaunsinger, W. S.; Von Dreele, R. B. *Solid State Ionics* **1988**, *26*, 47.

(7) Gamble, F. R.; Silbernagel, B. G. *J. Chem. Phys.* **1975**, *63*, 2544.

(8) Reikel, C. *Prog. Solid State Chem.* **1980**, *13*, 89.

(9) McMillian, P. F.; Cajipe, V.; Molinié, P.; Quinton, M. F.; Gourlaouen, V.; Colombet, P. *Chem. Mater.* **1991**, *3*, 796.

(10) Young, Jr., V. G.; McKelvy, M. J.; Glaunsinger, W. S.; Von Dreele, R. B. *Chem. Mater.* **1990**, *2*, 75.

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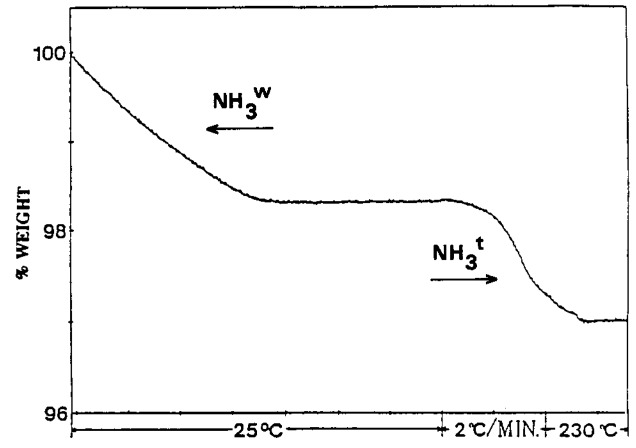

Figure 1. Typical TGA curve for the thermal deintercalation of $\mathrm{Na^+_{0.25}(NH_3^t)_{0.12}(NH_3^w)_{0.16}TiS_2^{0.25-}}$, where NH_3^t and NH_3^w represent more tightly and more weakly bound NH_3, respectively. Over 100 TGAs of $\mathrm{Na^+_{0.25}(NH_3)_{y'}TiS_2^{0.25-}}$, $0.12 < y' < 0.56$, consistently yielded the stable intermediate intercalate $\mathrm{Na^+_{0.25}(NH_3^t)_{0.12\pm0.01}TiS_2^{0.25-}}$, demonstrating the reproducible nature of the intermediate.

atmosphere conditions.[11,13] The results herein reflect multiple analyses of 20 individual sample preparations, all of which were reproducible within experimental error. Intercalate stoichiometry was determined using thermogravimetric analysis (TGA), as described previously.[11,13] Debye–Scherrer X-ray powder diffraction (XPD) data were collected for fully ammoniated and partially and completely NH_3 deintercalated samples contained in sealed 0.3-mm-diameter Pyrex capillaries. Materials containing 0.25 mol of Na^+/mol of TiS_2 were chosen for this investigation to avoid the co-intercalation of NH_4^+, which occurs for metal–NH_3 intercalates having a charge transfer less than 0.25 mol of e^-/mol of TiS_2,[13] and to maximize the NH_3/Na^+ ratio. The particle size of the resulting intercalates was of the order of tens of microns in diameter.

The fully intercalated material, equilibrated under 500 Torr of NH_3, has a stoichiometry of $\mathrm{Na^+_{0.25}(NH_3)_{0.75}TiS_2^{0.25-}}$. Gas evolution during thermal deintercalation, which was complete by 230 °C, occurred in two steps, and all the evolved gas was condensable at −196 °C. Mass spectrometric analysis showed that only NH_3 was liberated during both steps. A typical TGA curve for $\mathrm{Na^+_{0.25}(NH_3)_yTiS_2^{0.25-}}$ is shown in Figure 1. At ambient temperature, the more weakly held NH_3 (NH_3^w) deintercalates to form $\mathrm{Na^+_{0.25}(NH_3^t)_{0.12\pm0.01}TiS_2^{0.25-}}$. NH_3^t represents the remaining, more tightly held NH_3. This species is not removed until the temperature is increased above 90 °C. XPD of the resulting $\mathrm{Na^+_{0.25}TiS_2^{0.25-}}$ is in good agreement with the known 6R, stage-II structure of similar $\mathrm{Na^+_xTiS_2^{x-}}$ intercalates.[14]

XPD data for the fully intercalated material can be completely indexed as a 3R-type structure, with reflection intensities comparable to those for ammoniated TiS_2.[13] This indicates the stacking of the [S–Ti–S] layers rearranged during intercalation to provide trigonal prismatic interlayer guest sites, as previously observed for $\mathrm{(ND_4^+)_{0.22}(ND_3)_{0.34}TiS_2^{0.22-}}$.[6] The occupied-layer expansion (OLE) of 3.35 Å for the fully intercalated material is comparable to that for $\mathrm{(ND_4^+)_{0.22}(ND_3)_{0.34}TiS_2^{0.22-}}$,[6] as shown in Table I. This suggests that NH_3 in $\mathrm{Na^+_{0.25}(NH_3)_{0.75}TiS_2^{0.25-}}$ may have a structure and orientation similar to that observed for $\mathrm{(ND_4^+)_{0.22}(ND_3)_{0.34}TiS_2^{0.22-}}$, where ND_3 is effectively propping open the host layers. The small 0.14 Å difference in OLE between $\mathrm{(ND_4^+)_{0.22}(ND_3)_{0.34}TiS_2^{0.22-}}$ and $\mathrm{Na^+_{0.25}(NH_3)_{0.75}TiS_2^{0.25-}}$ is probably due to the additional NH_3 in the van der Waals (vdW) gap of the latter compound.

Table I. Cell Constants for Selected Intercalation Compounds

compound	*a* (Å)	*c* (Å)	OLE (Å)
$\mathrm{Na^+_{0.25}(NH_3)_{0.75}TiS_2^{0.25-}}$	3.426(1)	27.14(1)	3.35
$\mathrm{Na^+_{0.25}(NH_3^t)_{0.12}TiS_2^{0.25-}}$ [a]	3.421(5)	38.12(3)	1.32
$\mathrm{Na^+_{0.25}TiS_2^{0.25-}}$	3.417(2)	38.20(5)	1.34
$\mathrm{(ND_4^+)_{0.22}(ND_3)_{0.34}TiS_2^{0.22-}}$	3.417(1)	26.72(1)	3.21

[a] NH_3^t denotes tightly held NH_3.

XPD data for $\mathrm{Na^+_{0.25}(NH_3^t)_{0.12}TiS_2^{0.25-}}$ and $\mathrm{Na^+_{0.25}TiS_2^{0.25-}}$ are completely indexable as stage-II 6R structures. Their OLE's are experimentally indistinguishable, as shown in Table I, demonstrating that sodium is primarily responsible for host-layer separation. The pronounced drop in OLE from 3.35 Å for $\mathrm{Na^+_{0.25}(NH_3)_{0.75}TiS_2^{0.25-}}$ to 1.32 Å for $\mathrm{Na^+_{0.25}(NH_3^t)_{0.12}TiS_2^{0.25-}}$ suggests a 90° NH_3 reorientation, with the Na^+–host layer forces, which are primarily ionic, presumably forcing the compression of the vdW gap.

It is proposed that the following sequence of events provides a reasonable explanation of this unusual behavior. The initial deintercalation process, as illustrated in Figure 2 involves NH_3 propping open the layers, possibly with its pseudo-C_3 axis parallel to the host layers. During the progressive deintercalation of NH_3, the relative importance of Na^+–host layer attraction increases with decreasing NH_3 content until a threshold concentration is reached. At this concentration, insufficient NH_3 remains to hold the occupied vdW gaps open to 3 Å, and the $\mathrm{Na^+–TiS_2^{0.25-}}$ guest–host attractions initiate the collapse of the OLE to that observed for $\mathrm{Na^+_{0.25}TiS_2^{0.25-}}$. This can force the remaining NH_3^t to adopt a structure that is planar, or nearly planar, and parallel to the host layers.

The strong similarity between the XPD patterns of $\mathrm{Na^+_{0.25}(NH_3^t)_{0.12}TiS_2^{0.25-}}$ and $\mathrm{Na^+_{0.25}TiS_2^{0.25-}}$ suggest Na^+ resides in trigonal-prismatic guest sites for the ammoniate, as previously found for $\mathrm{Na^+_{0.25}TiS_2^{0.25-}}$.[14] The reoriented NH_3 also probably occupies trigonal-prismatic guest sites, with N at the site center. A probable NH_3 geometry would have the N–H bonds directed at the prism face centers, in which case the bonding would involve sp^2 hybridization of N. Figure 3 shows this configuration with the hydrogen atoms on the face center sites. The plausibility of such a structure follows from the calculated N–H (0.99 Å), H–S (2.7 Å), and S–N (2.9 Å) distances. The N–H distances are consistent with those found in crystalline NH_3.[6] The H–S distances are close to those associated with weak D···S hydrogen bonding in $\mathrm{(ND_4^+)_{0.22}(ND_3)_{0.34}TiS_2^{0.22-}}$.[6] The S–N distances are somewhat shorter than the vdW S–N distance of 3.2–3.3 Å,[16] which could result from a combination of electrostatic interlayer compressive forces due

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(11) Bernard, L.; McKelvy, M.; Glaunsinger, W.; Colombet, P. *Solid State Ionics* **1985**, *15*, 301.

(12) McKelvy, M. J.; Glaunsinger, W. S. *J. Solid State Chem.* **1987**, *66*, 181.

(13) McKelvy, M.; Bernard, L.; Glaunsinger, W.; Colombet, P. *Solid State Chem.* **1986**, *65*, 79.

(14) Bouwmeester, H. J. M.; Dekker, E. J. P.; Bronsema, K. D.; Haange, R. J.; Wiegers, G. A. *Rev. Chim. Miner.* **1982**, *19*, 333.

(15) Daumas, N.; Hérold, A., *C.R. Seances Acad. Sci., Ser., C* **1969**, *268*, 373.

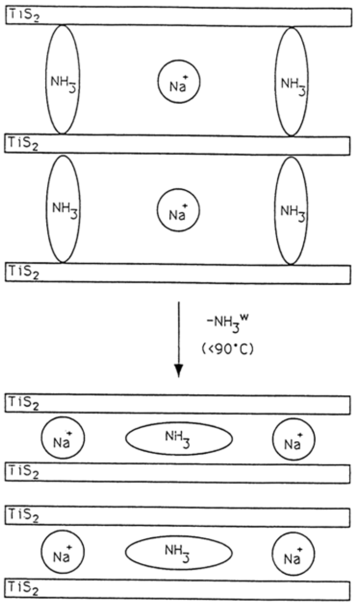

Figure 2. Schematic of the deintercalation and reorientation of NH_3 in $Na^+_{0.25}(NH_3)_{y'}TiS_2^{0.25-}$. The upper illustration is for the fully ammoniated sample ($y' = 0.75$), where planar NH_3 (represented by an ellipse) is assumed to be planar and perpendicular to the host layers by analogy to $(ND_4^+)_{0.22}(ND_3)_{0.34}TiS_2^{0.22-}$. Upon partial deintercalation to $y' = 0.12$, the occupied layer expansion decreases from 3.35 to 1.32 Å and NH_3 reorients from its original configuration to a planar, or near planar, geometry essentially parallel to the host layers, as shown in the lower illustration. The evolution of the NH_3 geometry between the initial and final configurations is unresolved. Note: The accompanying restaging (I → II) transition need not involve Na^+ transfer to neighboring galleries. Instead, the requisite restaging can be accomplished through the formation of Daumas–Hérold guest islands.[15]

to Na^+ and sp^2 hybridization of NH_3. Shorter S–N distances are expected for sp^2 hybridization, since the lone pair in the N $2p_z$ orbital is directed between intraplanar S sites. Moreover, a Slater orbital calculation indicates that 99.7% of the electron density of the N $2p_z$ orbital lies within a 1.2 Å radius, which is 0.35 Å smaller than the vdW radius of N and, hence, can help account for the reduced S–N distance for reoriented NH_3.

Differential scanning calorimetry (DSC) of $Na^+_{0.25}(NH_3)_{y'}TiS_2^{0.25-}$ to 300 °C exhibits a single endothermic peak below 90 °C that is associated with NH_3^w deintercalation (10.8 kcal/mol NH_3^w). This enthalpy is essentially the same as that for NH_3 in $(NH_4^+)_{0.22}(NH_3)_{0.23}TiS_2^{0.22-}$ (10.5 kcal/mol NH_3)[17], which suggests that these species are bound between the layers in a similar fashion. Except for a small baseline irregularity ($\approx$0.1 kcal/mol) the enthalpy associated with NH_3^t deintercalation is not observable within experimental error ($\pm$1 kcal/mol NH_3). This suggests that NH_3^t can be viewed as being "trapped" after NH_3^w deintercalation. The lack of an observable enthalpy change for NH_3^t deintercalation indicates its exothermic and endothermic components are nearly equal. It also demonstrates that NH_3^w substantially lowers the intercalate enthalpy while NH_3^t does not, which suggests that NH_3^t is less effective in stabilizing the intercalate (see Figure 3).

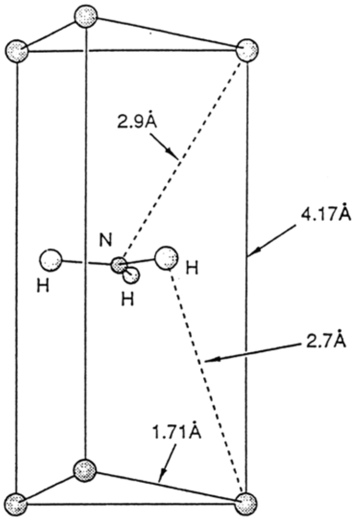

Figure 3. Possible model for NH_3^t in $Na^+_{0.25}(NH_3^t)_{0.12}TiS_2^{0.25-}$. NH_3^t is located in trigonal prismatic guest sites, with the N–H bonds directed at the prism face centers. In this configuration, the N orbitals used for N–H bonding would be sp^2 hybridized, and the electron lone pair on N would occupy a $2p_z$ orbital. The calculated N–H, H–S, and S–N distances are 0.99, 2.7, and 2.9 Å, respectively. In this model, 74% of the stage II trigonal prismatic guest sites are occupied, with some of the NH_3^t hydrogen positions quite close (2.7 Å) to the Na^+ positions. This suggests significant Na^+–H repulsions could be present. This is consistent with the DSC results, which indicate that NH_3^w stabilizes the intercalate by 10.8 kcal/mol NH_3 more than NH_3^t.

The planar structure of ammonia in $(ND_4^+)_{0.22}(ND_3)_{0.34}TiS_2^{0.22-}$ [6] and $Na^+_{0.25}(NH_3)_{0.12}TiS_2^{0.25-}$ underscores the inadequacy of viewing guest species as simply retaining their unintercalated molecular structure. Instead, the intercalated molecule is subjected to substantial guest–host and guest–guest interactions that may result in new structural arrangements. In particular, the above NH_3 guest species may closely resemble the planar transition-state structure associated with NH_3(g) inversion, which requires 5.9 kcal/mol NH_3 to occur.[18] Such an intercalant structure is feasible, since the distortion energy is only about half of the enthalpy decrease for NH_3 intercalation ($\approx$11 kcal/mol NH_3).[17] Although the evolution in NH_3 structure from the initial to the final planar configuration is unresolved, it is likely that the transition involves some pyramidal character.

Recent work in our laboratories indicates that NH_3^t is formed during the thermal deintercalation of $Na^+_x(NH_3)_yTiS_2^{x-}$ for $0.15 < x < 0.40$. Most importantly, the ratio NH_3^t:Na is 1:2 over this entire composition range. This indicates that during deintercalation more than one NH_3 per two sodiums can adequately oppose the sodium–host attractions. However, when the ratio reaches 1:2, sodium–host attractions dominate, resulting in partial collapse of the occupied vdW gaps and reorientation of NH_3.

Other monovalent metal–NH_3 systems intercalated into TiS_2 have also been investigated to determine if NH_3 reorientation is a general phenomenon. However, the only other system to exhibit evidence of NH_3 reorientation during deintercalation is silver–NH_3. Lithium forms intercalation complexes with NH_3, but there is no evidence

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(16) This distance was determined using 1.71 Å for the S radius and 1.55 Å for the vdW radius of N (Huheey, J. E. *Inorganic Chemistry: Principles of Structure and Reactivity*; Harper and Row: New York, 1972).

(17) McKelvy, M. J.; Glaunsinger, W. S. *J. Solid State Chem.* **1987**, *67*, 142.

(18) Townes, C. H.; Schawlow, A. L. *Microwave Spectroscopy*; Dover Publications, Inc.: New York, 1975.

for NH_3 reorientation during NH_3 deintercalation. The other alkali-metal intercalates, $M^+{}_xTiS_2{}^{x-}$ (M = K, Rb, Cs), have OLEs that are apparently too large to reorient NH_3. The NH_3 reorientation phenomenon is not expected to be limited to the above TiS_2 intercalates. Such behavior may well occur for other solvated-ion intercalates if a suitable balance of guest–guest and guest–host interactions can be achieved.

Finally, we wish to point out that it is also possible to interpret this phenomenon in terms of a change in H atom site preference around distinct N atom sites, where NH_3 is not viewed as a molecular guest, but rather as individual guest N and H atoms.[9] The applicability of the molecular versus atomic guest models will be the subject of a future publication.