Nature of Guest Species within Alkaline Earth–Ammonia Intercalates of Titanium Disulfide

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Alkaline earth–ammonia intercalated compounds of lamellar titanium disulfide have been investigated using thermogravimetric analysis, differential scanning calorimetry, X-ray photoelectron spectroscopy, evolved gas analysis, and inelastic neutron-scattering spectroscopy. Two energetically distinguishable molecular ammonia species, one weakly bound and the other complexed with alkaline earth cations, were found to coexist with metal and ammonium cations. The energies required to deintercalate these species are 13, 19, and 22 kcal/mol, respectively. Vibrational motions associated with complexed ammonia were observed in addition to those from uncomplexed ammonia. The weakly bound NH_3 exhibited vibrational bands at 290 and 345 cm^{-1}. The most prominent vibrational modes for the complexed ammonia were the NH_3 torsion and rock whose frequencies were 167 and 470 cm^{-1}, respectively, in the calcium intercalates. A change in the cation from Ca^{2+} to Sr^{2+} to Ba^{2+} resulted in a shift of the NH_3 rocking mode frequency from 470 to 460 to 425 cm^{-1}, respectively. In this work the nature of the guest species in TiS_2 has been thoroughly characterized, and strong evidence is presented for the existence of distinct molecular ammonia species.

Introduction

Graphite, lamellar oxides, and sulfides are often used as model compounds for the study of interfacial reactions. These materials consist of slabs of the host structure separated by solid state interfaces between the slabs that can be intercalated with metal and/or molecular guests. Such intercalation reactions are usually accompanied by oxidation of the guest species coupled with electron transfer to the host. The resulting intercalation compounds contain a monolayer or bilayer of guest cations and possibly neutral species sandwiched between negatively charged host slabs. Intercalation involves the replacement of weaker dipole–dipole and London forces between the slabs of the pristine host by stronger ion–dipole and dipole–dipole forces. The guest species in these interfaces can exhibit two-dimensional or three-dimensional type behavior depending on the relative strength of these interactions with the surface of the host slabs and with other guest species. In lamellar oxide materials strong ionic forces between the host slabs allow little flexibility for the guest species in that three-dimensional networks are usually formed.[1] The relatively weak forces between the slabs of lamellar titanium disulfide make it a good choice for the investigation of solvation chemistry in two dimensions and interactions at solid-state interfaces. TiS_2 consists of a hexagonal layer of titanium sandwiched between two hexagonal layers of sulfur. In this study the alkaline earth metals and ammonia have been chosen as the guest species to be incorporated into the van der Waals (vdW) gaps between the TiS_2 layers. In these model systems the metal cations serve as solutes and ammonia as the solvent. The reason for this choice of species is their chemical and structural simplicity as well as the stability of the complexes that are formed.

One of the first questions that must be addressed is the identity and concentration of guest species. In an ideal intercalation reaction guest species retain their identity upon entering the host compound. Originally it was thought that the intercalation of ammonia into TMDs involved only the insertion of NH_3 molecules.[2] More detailed studies indicate, however, that the intercalation of NH_3 into TMDs is accompanied by redox reactions, so that both NH_3 and NH_4^+ are usually found to be cointercalated into these hosts.[3,4] More recently a new model[5] based on ambient temperature magic-angle-spinning and variable-temperature pulsed NMR data was proposed, which suggests that NH_3 molecules decompose into nonmolecular hydrogen and nitrogen atoms upon entering TiS_2. In this study a single proton resonance line as well as spinning side bands, with a chemical shift intermediate between those of NH_3 and NH_4^+, was observed. It was proposed that nitrogen atoms reside within trigonal prismatic sites surrounded by rapidly exchanging hydrogen atoms in neighboring

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(1) Delmas, C. *Chemical Physics of Intercalation*; Legrand, A. P., Flandrios, S., Eds.; Plenum Press: New York, 1987; p 209.

(2) See, for example: Silbernagel, B. G.; Dines, M. B.; Gamble, F. R.; Gebhard, L. A.; Whittingham, M. S. *J. Chem. Phys.* **1976,** *65,* 1906.

(3) Schöllhorn, R.; Zagefka, H. D. *Angew. Chem., Int. Engl. Ed.* **1977,** *16,* 199.

(4) McKelvy, M. J.; Glaunsinger, W. S. *J. Solid State Chem.* **1987,** *67,* 142. McKelvy, M. J.; Glaunsinger, W. S. *Solid State Ionics* **1987,** *25,* 287.

(5) McMillan, P. F.; Cajipe, V.; Molinie, P.; Quinton, M. F.; Gourlaouen, V.; Colombet, P. *Chem. Mater.* **1991,** *3,* 796.

sites, whereas earlier reports had placed NH_3 molecules within these trigonal prismatic sites.[6,7]

Recent studies indicate that metal–ammonia solutions of lithium and alkaline earths trapped in the vdW gaps of TiS_2 form solvation complexes.[6,8] Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) studies revealed three distinct species derived from NH_3.[8] X-ray photoelectron spectroscopy (XPS) showed that these species coexist in the vdW gaps and are not a consequence of thermal treatment. Systematic powder neutron and X-ray diffraction studies indicate that the guest molecules are intercalated as monolayers within the vdW gaps and separate the TiS_2 host slabs by 3.0 Å over a wide intercalant concentration range.[8] This separation is the result of the presence of NH_3 which props the slabs apart. The alkaline earth–ammonia intercalates were found to adopt a structure similar to that of lithium–ammonia intercalates,[6] in which the host layers are shifted relative to one another to form a trigonal prismatic arrangement of sulfur atoms from adjacent host slabs. For both $Li(NH_3)TiS_2$ and $Ca(NH_3)TiS_2$ the diffraction patterns could be indexed as a trigonal cell (space group $R3m$) with lattice constants $a = 3.424$ Å, $c = 26.718$ Å and $a = 3.42$, $c = 26.2$ Å, respectively. In the presence of NH_3 the cations reside between two sulfur atoms. NH_3 and NH_4^+ are statistically distributed over the trigonal prismatic sites in this structure. The orientation of NH_3 is such that two of its hydrogen atoms are directed at sulfur atoms, one from each of the adjacent host slabs forming the trigonal prismatic site[6,7] whereas its pseudo-C_3 axis appears to lie parallel to the basal planes of the host. In contrast the hydrogen atoms on the NH_4^+ were taken to be spherically disordered.[7,9]

In this paper we describe the results of an investigation of the alkaline earth–ammonia intercalation compounds of TiS_2 using several experimental techniques in an attempt to provide answers to the following questions: (i) the number and nature of the guest species, (ii) the concentration of each guest species, and (iii) the nature and strength of the interactions between the guest species. We will also compare the alkaline earth–ammonia intercalates with the ammonium–ammonia and ammonium systems reported[3,4,10] previously.

Experimental Details

The synthesis of stoichiometric TiS_2 from the elements and that of the various metal–ammonia intercalates was carried out as described previously.[8,11] All samples were handled, prepared, and investigated under rigorous inert-atmosphere conditions because of their moisture and air sensitivity.[8]

Single crystals of TiS_2 were grown by vapor-transport techniques as described previously,[12] except that sulfur was used as the transporting agent. A charge of TiS_2 powder was mixed with sulfur and loaded into a quartz ampoule. The ampule was placed in a Marshall furnace with the charge end at 750 °C and the growth end at 650 °C.

The stoichiometry of the samples was determined using a Perkin-Elmer TGS-2 TGA system. The sulfur content of TiS_2 was measured by oxidation to TiO_2 using oxygen gas at temperatures up to 950 °C. The relative amount of NH_3-related species in the intercalates was determined using argon as the carrier gas, and the temperature was limited to a maximum of 350 °C since TiS_2 loses sulfur above this temperature in the absence of excess free sulfur.

DSC measurements were performed to estimate the deintercalation enthalpy of each NH_3-derived species. A Perkin-Elmer DSC-4 system was used with argon carrier gas to match the thermal conductivity of the evolved species.

The quantity and identity of the various volatile species was established by evolved gas analysis (EGA), which consisted of a vacuum line equipped with a Baratron pressure sensor and a quadrupole mass spectrometer (Hiden Analytical Laboratories, model HAL-201). The vapor pressure of NH_3 over the intercalates was also determined by this technique.

XPS was used to investigate the near-surface nitrogen atoms of complexed NH_3 and of NH_4^+ using a KRATOS XSAM-800 spectrometer. Two different cathodes (aluminum and magnesium) were utilized in the investigation in order to distinguish XPS events from Auger events.

The vibrational modes of the NH_3 were studied by inelastic neutron-scattering spectroscopy (INS) primarily because it is very difficult to perform infrared absorption or Raman scattering spectroscopy on these compounds because of their metallic nature. In the INS experiments powder samples of approximately 3–5 g were sealed in aluminum sample cans in the shape of a cylindrical annulus. For the orientation dependence of the INS spectra an oriented array of 50 calcium–ammonia intercalated TiS_2 single crystals (typical size 10 × 10 × 0.5 mm) was mounted onto an aluminum plate and sealed within a cylindrical sample container. The samples were cooled in a closed-cycle He refrigerator. The INS vibrational spectra were collected at 15 K on the filter difference spectrometer (FDS) at the Los Alamos Neutron Scattering Center (LANSCE) of Los Alamos National Laboratory.[10,13] Data analysis was carried out using methods[13,14] described previously.

Results and Discussion

Evidence for Coexistence of Distinguishable Species. Thermogravimetric analysis and vapor pressure measurements coupled with mass spectrometry were used to determine the identity and relative concentration of gases evolved during the deintercalation process. Thermograms of three different calcium–ammonia intercalates obtained by TGA are shown in Figure 1. An typical plot of the evolved gas pressure as a function of temperature is shown in Figure 2 for a strontium–ammonia intercalate. The amount of gas evolved yields an intercalate stoichiometry that is comparable with the more precise TGA results. The compounds exhibit as many as three weight-loss events depending on the number of different ammonia species in the intercalate. The number of such events and the amount of weight loss associated with each is strongly dependent on the cation concentration. The results of DSC experiments discussed below corroborate this finding. The identity of each evolved-gas species and the variation of their relative concentrations with cation content of the intercalates are discussed below.

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

(7) Young, Jr., V. G.; McKelvy, M. J.; Glaunsinger, W. S.; Von Dreele, R. B. *Chem. Mater.* **1988**, *26*, 47.

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

(9) O'Bannon, G. W.; Glaunsinger, W. S.; Marzke, R. F. *Solid State Ionics* **1988**, *26*, 15.

(10) Glaunsinger, W. S.; McKelvy, M. J.; Larson, E. M.; Von Dreele, R. B.; Eckert, J.; Ross, N. L. *Solid State Ionics* **1989**, *34*, 281.

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

(12) Schäfer, H. *Chemical Transport Reactions*; Academic Press: New York, 1964.

(13) Taylor, A. D.; Wood, E. J.; Goldstone, J. A.; Eckert, J. *J. Nuclear Instrum. Methods Phys. Res.* **1984**, *221*, 408.

(14) Sivia, D. S.; Vorderwish, P.; Silver, R. *J. Nuclear Instum. Methods Phys. Res.* **1990**, *A290*, 492.

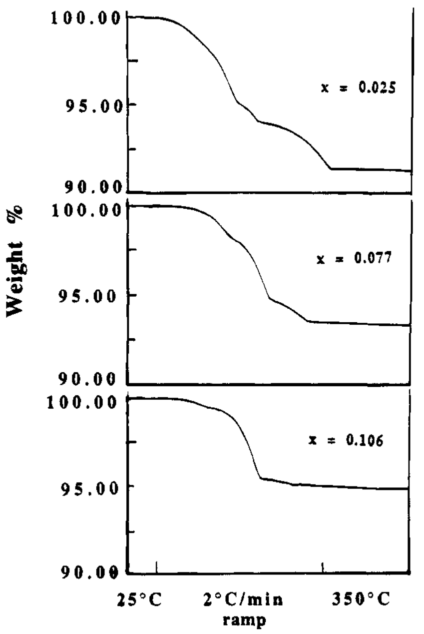

Figure 1. TGA thermogram for a calcium−ammonia intercalate of TiS_2 having different calcium concentrations. Three distinct weight losses are observed due to volatile species derived from intercalated ammonia: uncomplexed NH_3, complexed NH_3, and NH_4^+. The stoichiometries of the compounds are $(NH_3^w)_{0.37}[Ca^{2+}_{0.025}(NH_3^s)_{0.08}](NH_4^+)_{0.19}TiS_2^{0.24-}$, $(NH_3^w)_{0.11}[Ca^{2+}_{0.077}(NH_3^s)_{0.23}](NH_4^+)_{0.09}TiS_2^{0.24-}$, and $(NH_3^w)_{0.05}[Ca^{2+}_{0.106}(NH_3^s)_{0.29}](NH_4^+)_{0.04}TiS_2^{0.25-}$, respectively. Compounds containing Sr^{2+}, Ba^{2+}, and Yb^{3+} exhibit similar behavior. NH_3^w and NH_3^s represent weakly bound (uncomplexed) and more strongly bound (complexed) NH_3, respectively.

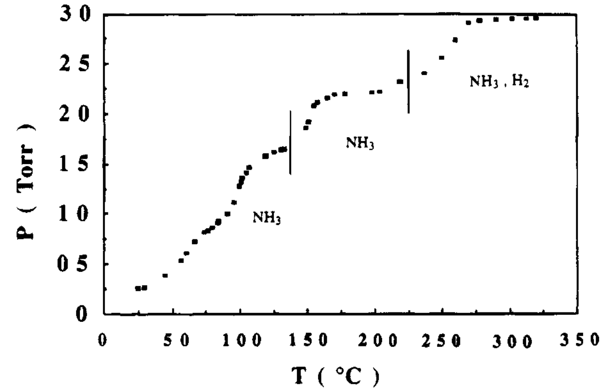

Figure 2. Pressure of volatile species deintercalated as a function of temperature, as determined by EGA. The species evolved are indicated. The onset of noncondensable gases due to decomposition of NH_4^+ occurs above 200 °C. The sample used in this experiment was $(NH_3^w)_{0.25}[Sr^{2+}_{0.032}(NH_3^s)_{0.18}](NH_4^+)_{0.15}TiS_2^{0.21-}$.

The identity of the gaseous species that were deintercalated and subsequently trapped in vessels immersed in liquid nitrogen was established by mass spectrometry. Gas samples were examined at the plateau of each step in Figure 2. Figure 3 shows the mass spectra of condensable and noncondensable gases. The experiments indicate that only NH_3 is evolved in the first two steps, weakly bound in the former and strongly bound in the latter. The fragmentation pattern of the mass spectrum of the condensable gases is characteristic of NH_3. The vapor pressure of the weakly bound NH_3 in the alkaline earth−ammonia intercalates is approximately 2−3 Torr at ambient temperature which is lower than that of NH_3 in $(NH_3)_{0.54}(NH_4^+)_{0.25}TiS_2^{0.25-}$ at 13 ± 1 Torr. The vapor pressures of the other species are negligible. The strongly bound NH_3 did not desorb from the sample until the temperature reached 130 °C.

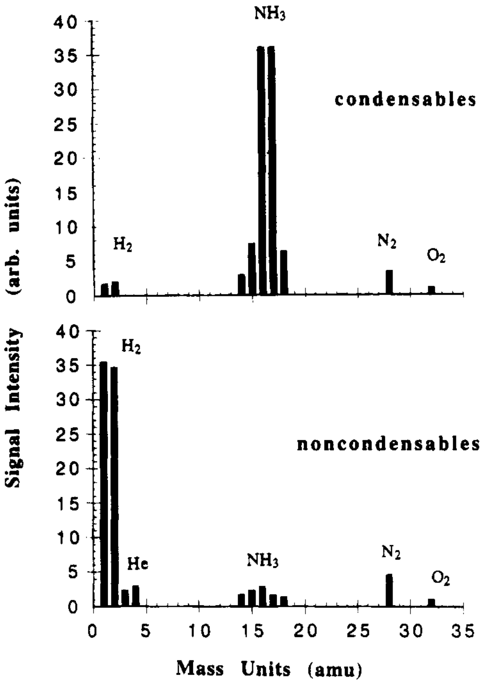

Figure 3. Typical mass spectrograms used to identify gases evolved from alkaline earth−ammonia intercalates of TiS_2. (a) The condensable portion is ammonia. (b) The noncondensable portion is hydrogen. Traces of nitrogen and oxygen are present from residual amount of air present. Traces of hydrogen and water are from the instrument chamber walls. The helium present may have leaked from stopcocks. Note that H_2S is not present.

It is also noteworthy that no peaks attributable to H_2S were found. This result indicates that the host material has not been attacked by moisture and demonstrates that the compositional integrity of the host was maintained during the experiments. Moisture contamination can also result in the formation of an excessive amount of NH_4^+ in the samples. The maximum amount of NH_4^+ that can form from the redox reaction between NH_3 and TiS_2 is 0.25 mol of NH_4^+/mol of TiS_2,[15] and this level was never exceeded in our samples. On further heating the decomposition of NH_4^+ and its deintercalation near 200 °C were indicated by the evolution of hydrogen gas. A 2:1 mole ratio of NH_3 to H_2 is evolved in the third step in quantitative agreement with guest−host redox reactions.[4,16] The evolution of H_2 in the noncondensable portion of the evolved gases was confirmed by mass spectrometry. Decomposition and deintercalation of NH_4^+ in TiS_2 proceeded in a single step, in contrast to TaS_2 where NH_3 and H_2 evolve at different temperatures.[17,18]

Since two distinct NH_3 species as well as NH_4^+ exist in the alkaline earth−ammonia intercalates of TiS_2 they can be described as $(NH_3^w)_u[M^{2+}_x(NH_3^s)_{nx}]\,(NH_4^+)_{0.25-2x}TiS_2^{0.25-}$ for $x \leq 0.125$, where NH_3^w and NH_3^s represent

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(15) McKelvy, M. J.; Dunn, J. M.; Young, Jr., V. G.; Glaunsinger, W. S. *Solid State Ionics* **1989**, *32/33*, 174.

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

(17) Diebolt, L. A.; Glaunsinger, W. S., McKelvy, M. J.; Eckert, J., unpublished.

(18) Moyes, R. B. *Hydrogen Effects in Catalysis*; Paal, Z., Menon, K., Eds.; Dekker: New York, 1988, p 583.

weakly bound (uncomplexed) and more strongly bound (complexed) NH_3, respectively. The quantities u and x are the concentrations of weakly bound ammonia and alkaline earth cation, respectively, and n is the coordination number of the metal ion. The concentrations of weakly bound NH_3 and of NH_4^+ decreased with increasing intercalated metal content whereas the concentration of strongly bound NH_3 increased. Furthermore, the concentration of weakly bound NH_3 depends on the history of the sample (i.e., the temperature and partial pressure of NH_3 over the sample during equilibration). The NH_4^+ concentration within the sample is strongly dependent on the metal cation concentration because of charge compensation during the redox reaction.[16] When there is not enough metal to contribute at least 0.22–0.25 mol of electrons per mol of host, NH_3 molecules are oxidized to NH_4^+ to achieve this degree of charge transfer. A feasible mechanism describing the oxidation of NH_3 and subsequent formation of NH_4^+ has been described previously.[3,4] The relatively high potential required to oxidize NH_3 and the ion–ion repulsion between NH_4^+ in the host limits the concentration of electrons donated to the host. Stronger reducing species such as alikali or alkaline earth metals can contribute as much as ~2 mol of electrons/mol of host.

It is interesting to note that the molecular ratio of strongly bound ammonia to the intercalated cation was found to be constant over a wide range of metal concentrations. This observation strongly indicates the existence of stable solvation complexes between the alkaline earth cations and ammonia with distinct coordination numbers which is confirmed by our INS experiments to be discussed below. The value of n can be 2, 3, or 6 depending on the metal cation.[8] These two-dimensional coordination numbers fit well with the hexagonal symmetry of the host basal plane. The smaller cations such as calcium and ytterbium[8] favor coordination numbers of 3 and 2, whereas a larger cation like strontium favors 6 and 3. Other interesting findings are that at low metal concentrations the complexes favor higher coordination numbers and that they undergo transitions to lower coordination numbers above certain discrete concentrations. It appears that repulsive interactions between ammonia from different complexes become more important as the complexes are crowded together at high metal concentrations. Overall, the total content of intercalants appears to decline as the concentration of intercalated metal ions increases. This may be a reflection of the inefficient packing of molecules in the host basal plane because of the presence of metal–ammonia complexes within the vdW gaps. These trends are illustrated in Figure 4 for the calcium–ammonia intercalates.

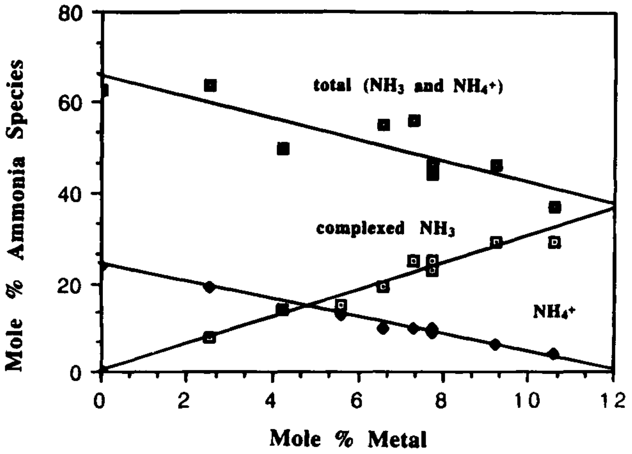

Figure 4. The concentrations of various ammonia-derived species as a function of calcium concentration (x) in calcium–ammonia intercalates of TiS_2. The amount of complexed NH_3 increases with metal content, varying as $3x$. The NH_4^+ concentration varies approximately as $0.23 - 2x$. The total NH_3/NH_4^+ content generally decreases with increasing metal content. The scatter in the total ammonia content reflects the large variation in the amount of uncomplexed NH_3, which strongly depends on the history of the sample.

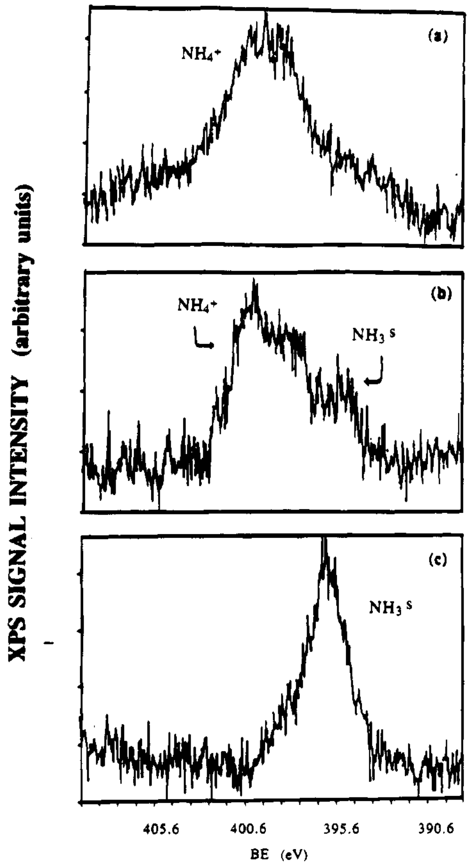

Figure 5. Nitrogen 1-s XPS spectra of metal–ammonia intercalates showing NH_4^+ and complexed NH_3. The uncomplexed NH_3 vaporized in the vacuum chamber and hence was not observed. The compounds are (a) $(NH_3^{w})_{0.39}(NH_4^+)_{0.24}TiS_2^{0.24-}$, (b) $(NH_3^{w})_{0.29}[Yb^{3+}{}_{0.032}(NH_3^{s})_{0.08}](NH_4^+)_{0.12}TiS_2^{0.22-}$, and (c) $[Ca^{2+}{}_{0.267}(NH_3^{s})_{0.59}]TiS_2^{0.534-}$.

In the above analyses the samples were heated to examine the evolved gases. An important question that arises from this approach is whether the second and third species observed in the TGA and EGA experiments were generated as a result of heating the samples. The evidence that the various species derived from ammonia do indeed coexist within the intercalates is provided by the XPS spectra shown in Figure 5. Samples were investigated by XPS prior to any heat treatment. The environment of the nitrogen atom in the NH_3-derived species was probed by monitoring the binding energy of the nitrogen-1s photoelectrons which range from 397 to 408 eV.[19] The binding energies of the photoelectrons for the complexed NH_3 and for NH_4^+ were 396 eV and

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(19) Wagner, C. D.; Riggs, W. M.; Davis, L. E.; Moulder, J. F.; Muilenberg, G. E. *Handbook of X-Ray Photoelectron Spectroscopy*; Perkin-Elmer Corp.: Minnesota, 1979.

401 eV, respectively. The former is somewhat less than the binding energy 399.8 eV for NH_3 in $Co(NH_3)_6Cl_3$, whereas the value for the latter is very close the binding energy for NH_4^+ in NH_4NO_3. These observations clearly suggest that the positive charge is localized on NH_4^+, which makes the escape of electrons more difficult than for complexed NH_3 where the positive charge is exerted by a neighboring alkaline earth cation. The uncomplexed NH_3 could not be observed in these experiments because of its volatility and because the samples could not be cooled to reduce vapor pressures sufficiently low relative to the operating pressure of the XPS at 10^{-8} Torr. The binding energy for electrons from uncomplexed NH_3 should be lower than for those from complexed NH_3 because there are no neighboring positive charges. Since NH_3^s is resolvable from NH_4^+, one should therefore be able to resolve NH_3^w from NH_4^+. Our XPS results do therefore show that there are at least two nitrogen atoms with different environments consistent with the coexistence of at least one NH_3 species and NH_4^+ in TiS_2. This finding is in contrast to a recently proposed model[5] which suggests that intercalated NH_3 dissociates into atomic N and H and that the latter occupies only one type of site. If this model were correct only one N-1s signal should have been observed in this XPS study.

Guest–Host and Guest–Guest Interactions. To gain a better understanding at the molecular level of the intercalation processes described above, it is useful to determine the relative strength of the interactions between different intercalated NH_3 species (guest–guest) and between NH_3 species and the host TiS_2. In particular, the amount of energy required for deintercalation of the different NH_3 species gives an indication of how strongly they are held within the host and the molecular vibrational frequencies of the intercalants provide a measure of both the guest–guest and guest–host interactions as well as the intramolecular forces.

Both NH_3 and NH_4^+ within the calcium–ammonia and strontium–ammonia compounds are distinguishable energetically in DSC measurements.[8] As an example, the DSC thermogram for three calcium–ammonia intercalates is shown in Figure 6. The three thermal events observed in these experiments agree with the TGA results. The sawtooth-like line shape of the events is characteristic of vaporization. The appearance to two overlapping peaks in the last event is the result of the mismatch of thermal conductivity between the evolved hydrogen gas and the argon carrier gas. No thermal event that would signal the occurence of a structural phase transition was evident in the DSC measurements. Such events produce sharp symmetric peaks in the DSC trace. Because of the relatively weak interaction between Ba^{2+} and NH_3, DSC could not resolve the deintercalation of uncomplexed from complexed NH_3. The DSC results show that uncomplexed NH_3 has a deintercalation enthalpy ranging from 10.5 to 13 kcal/mol of NH_3, depending on the system,[3,8] whereas that of the complexed NH_3 was 19 ± 2 kcal/mol of NH_3.[8] As expected, NH_4^+ has the highest deintercalation enthalpy of 22 ± 2 kcal/mol of NH_4^+.

The above results indicate that the guest–guest and guest–host interactions experienced by each species is different. Deintercalation enthalpies, however, give only a measure of how much energy is required to expel the various species from the host but do not give a direct measure of the individual intermolecular interactions affecting the ammonia species. The deintercalation enthalpy includes contributions from hydrogen bonding, diffusion, $M-NH_3$ bond cleavage, electrostatic and elastic energies, and desorption. Furthermore, studies performed using DSC do not have sufficient energy resolution to differentiate between NH_3 complexes of different alkaline earth cations.

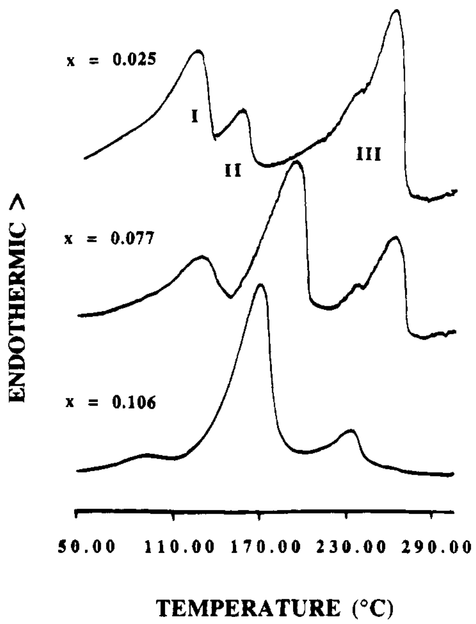

Figure 6. DSC thermograms for the same calcium–ammonia intercalates as in Figure 1. Three endotherms were observed, each corresponding to heat gain associated with the events shown in Figure 1. The ammonia species are energetically distinguishable. The third event that appears to be two overlapping peaks is an artifact from thermal conductivity mismatch between argon carrier gas and evolved hydrogen. The other alkaline earth ammonia intercalates behave similarly.

The relative strengths of guest–guest and guest–host interactions within the alkaline earth–ammonia intercalates were investigated by vibrational spectroscopy using INS. Three sets of experiments with systematic variations were performed in order to assign the vibrational modes in the INS spectra. In the first experiment calcium–ammonia intercalates were studied having different calcium concentrations $x = 0.032$, 0.065, and 0.099 with the attendant differences in ammonia species concentrations in order to differentiate the modes associated with the complexed NH_3 from those of uncomplexed NH_3 and NH_4^+. This strategy was used because the rapid exchange[20] between H and D on ammonia of 3.2×10^8 mol L^{-1} s^{-1} would eliminate the possibility of using selective deuteration to differentiate between the different types of ammonia species.

The other two sets of experiments were conducted to further investigate the behavior of the complexed NH_3. In the second experiment, the cation was systematically changed from Ca^{2+} to Sr^{2+} to Ba^{2+} while keeping the cationic concentration constant at $x = 0.10$. This metal concentration was chosen to study the complexes with predominantly 3-fold coordination. The vibrational modes of the complexed NH_3 are expected to shift in

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(20) Arnaut, L. G. *Proton Transfer in Hydrogen-Bonded Systems*, Bountis, T., Ed.; Plenum Press: New York, 1992; pp 281–295.

frequency for different cations. Finally, to facilitate assignment of the INS bands spectra were collected on an oriented array of 50 calcium–ammonia intercalated TiS_2 single crystals. The latter approach was used because the INS band intensities vary with the orientation of the neutron beam relative to the direction of the atomic displacements which contribute to a particular vibrational mode.[21] More precisely, the INS cross section contains terms of the form $(\mathbf{Q}\cdot\mathbf{u}_i)^2$, where u_i refers to the displacements of each of the atoms involved in a particular vibrational mode and $\mathbf{Q} = \mathbf{k}_i - \mathbf{k}_f$, where $\mathbf{k}_i$ and $\mathbf{k}_f$ are the wave vectors of the incident and scattered neutrons, respectively, is the neutron-scattering momentum transfer vector. Spectra obtained with the $\mathbf{Q}$ vector perpendicular or parallel to the basal plane will select vibrational modes with displacements predominantly perpendicular or parallel to $\mathbf{Q}$, respectively. Since in these experiments $\mathbf{k}_f$ is small[13] compared to the momentum vector of the incoming neutrons, alignment of the incident beam parallel or perpendicular to the basal plane will produce the desired selectivity. However, because of the size of the incident beam and the rather coarse collimation in the spectrometer the intensities of the bands associated with displacements perpendicular to those selected by orientation relative to $\mathbf{Q}$ will not be exactly zero. A comparison of the INS spectra of the Ca^{2+}, Sr^{2+}, and Ba^{2+} intercalates is shown in Figure 7, and the INS spectra of the calcium–ammonia intercalate single-crystal array with the incident beam parallel and perpendicular to the basal plane are shown in Figure 8.

To make comparisons between the different compounds and intercalated molecular species, we will first discuss our proposed assignments of the INS bands in these compounds, which are summarized in Table 1. The identification of the INS bands is based on the well-known property of the INS cross section that vibrational modes involving large displacements of H atoms will generally have the highest intensity. We also utilize the results from the previous section which show that these compounds contain two types of NH_3 molecules. We first assign two fairly prominent bands to the (external) torsional motions of uncomplexed NH_3. Their frequencies are at 290 ± 4 and 345 ± 5 cm^{-1}, at 280 ± 4 and 350 ± 5 cm^{-1}, and at 290 ± 4 with 330 ± 5 and 345 ± 5 cm^{-1}, in the Ca^{2+}, Sr^{2+}, and Ba^{2+} intercalates, respectively. The intensities of these bands vary as expected with the amount of uncomplexed NH_3 present in the series of Ca^{2+} compounds and do not exhibit a strong orientational dependence relative to the host basal plane. This NH_3 species is assumed to be bound within the host by weak N–H···S hydrogen bonds formed between it and the adjacent host slabs.[6,7] These hydrogen bonds are rather weak so that large-amplitude librations relative to the basal planes can occur.

In the related compound $(NH_4^+)_{0.20}(NH_3)_{0.36}TiS_2^{0.20-}$ torsional modes were found for the NH_3 molecules at frequencies of 295 and 355 cm^{-1}, which appeared to be related to those in pure solid NH_3 where librations about the 3-fold axis, $R_z(A)$ and $R_z(F)$, are assigned at lower frequencies, i.e., 248 and 320 cm^{-1}.[10] This suggests that the N–H···S hydrogen bonds of NH_3 intercalated in TiS_2 are in fact somewhat stronger than the N–H···N hydrogen bonds in solid NH_3, although both are rather weak. The strength of interactions of the uncomplexed NH_3 with TiS_2 in the alkaline earth–ammonia intercalates

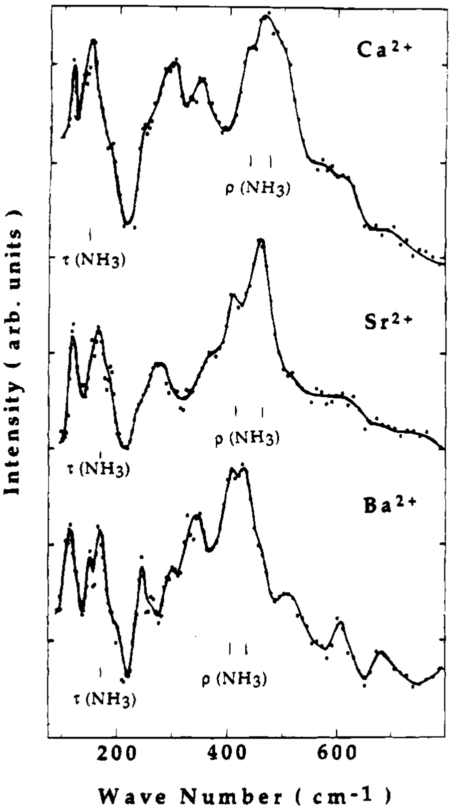

Figure 7. INS spectra for Ca–ammonia, Sr–ammonia, and Ba–ammonia intercalates. Each compound has the cation concentration fixed at $x = 0.10$ and similar NH_3 concentrations. Note the systematic downward shift in frequency of the rocking mode for the complexed ammonia: 470 cm^{-1} (Ca^{2+}), 460 cm^{-1} (Sr^{2+}), and 425 cm^{-1} (Ba^{2+}). The shift for the torsional mode near 167 cm^{-1} is smaller.

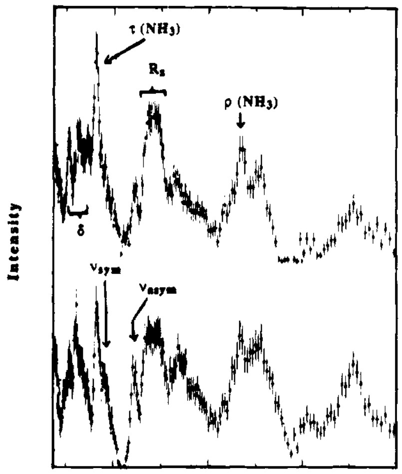

Figure 8. INS spectra for an oriented array of 50 calcium–ammonia TiS_2 single crystals with the incident neutron beam perpendicular to the crystal basal planes (top) and parallel to the basal planes (bottom). Note the change in relative intensity of the various vibrational bands in each spectrum. Some assignments are indicated according to Table 1. R_z refers to 3-fold axis rotation of uncomplexed ammonia, the other labels designate modes of the complex.

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(21) Bee, M. *Quasielastic Neutron Scattering: Principles and Applications in Solid State Chemistry, Biology and Materials Science*; Adam Hilger: Bristol, 1988.

Table 1. INS Vibrational Bands (in cm^{-1}) for Ammonia Species in Alkaline Earth–Ammonia Intercalation Compounds of TiS$_2$ and Probable Assignments (See Text for Details)

	M		
assignment[a]	Ca	Sr	Ba
	85	85	
	108		107
δ(N–M–N) (complex), ∥ ν_4(E′)	119	122	116
δ(N–M–N) (complex), ⊥, ν_2(A″$_2$)	145	154	150
τ(NH$_3$) (complexed)	165	167	168
	180		
ν(M–N) (complex), symm, ν_1(A′$_1$)	193	191	
ν(M–N) (complex), asymm, ν_3(E′)	245		249
τ(NH$_3$) (uncomplexed), R_z(A)	290	280	290
τ(NH$_3$) (uncomplexed), R_z(F)	345	350	330
			350
ϱ(NH$_3$) (complex), ⊥	435	410	405
ϱ(NH$_3$) (complex), ⊥	470	460	425
	510		515
	580	585	605
⊥	685		

[a] The mode numbers and symmetry species refer to the modes of a planar M–NH$_3$ complex, A″$_2$, A′$_1$, and E′ symmetries are notations for the D_{3h} point group. R_Z(A) and R_Z(F) are analogies to the assignments for solid ammonia. The mode notations are δ = deformation, τ = torsion, ν = stretching, ϱ = rocking.

is therefore comparable with that in (NH$_4^+$)$_{0.20}$(NH$_3$)$_{0.36}$TiS$_2^{0.20-}$. This observation agrees with the correlation of hydrogen bond strength vs nitrogen-to-nitrogen distance by Lautie et al.,[22] who suggest that a N–H⋯S hydrogen bond is equal in strength to an N–H⋯N hydrogen bond with the N–N distance increased by 0.36 Å. The N⋯S distances in the ammonia–titanium disulfide systems range from 3.57 to 3.65 Å,[6,7] whereas the N⋯N distance in solid ammonia at low temperatures is 3.33 Å. An equally strong N–H⋯S bond is predicted therefore to have a N⋯S distance of 3.69 Å, which is longer than the observed distance. However, an often neglected contribution to the strength of a hydrogen bond is the polarizability of the electronegative atoms.[23,24] Sulfur, being more polarizable than nitrogen, contributes more electron density to the hydrogen bond than nitrogen which may account for the shorter observed distance.

The vibrational modes of complexed NH$_3$ do not, of course, have a counterpart in the spectra of ammonia-intercalated TiS$_2$ without alkaline-earth cations and can thus be identified. In particular, their INS band intensities increase as the concentration of Ca^{2+} and complexed NH$_3$ is increased. The vibrational motions of the complex can be conveniently separated into those that are primarily associated with the ligand NH$_3$ and those involving the framework of the entire complex. Deformations of the entire metal–ammonia complex would be expected[25] at low frequencies, which leads to the assignment of framework vibrational modes to bands in the ranges 116–122 and 145–154 cm^{-1}. Orientation-dependent studies show that these bands involve motions parallel and perpendicular to the basal plane, respectively. They are therefore attributed to the in-plane deformation (ν_4) and the out-of-plane deformation (ν_2), which are shown schematically in Figure 9, where the ammonia ligand is represented by a point mass. The above finding suggests that it requires less energy to move parallel to the basal plane than against the TiS$_2$ slabs as anticipated.

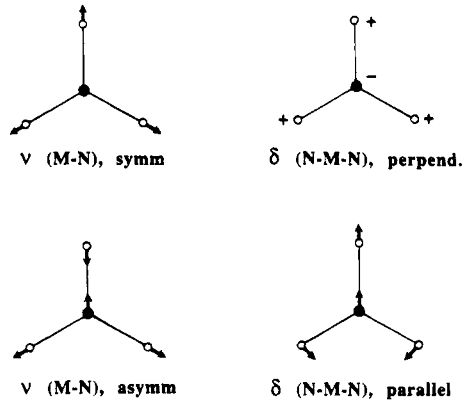

Figure 9. Schematic of the skeletal vibrations of the planar alkaline earth–ammonia complexes. NH$_3$ is represented by a point mass. ν represents metal–ammonia stretching parallel to the basal planes of the host; δ(N–M–N) ⊥ and ∥ are framework deformations of the complex perpendicular and parallel to the basal plane, respectively.

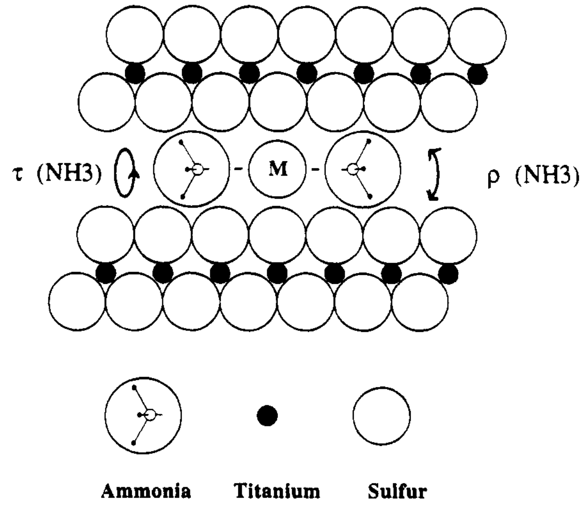

Figure 10. Edge-on view of the host slabs with intercalated alkaline earth–ammonia complexes. τ is the torsional motion of the ammonia with the axis of rotation parallel to the basal planes and ϱ is the rocking motion of NH$_3$, against the host slabs.

The torsion about the 3-fold axis of the complexed NH$_3$ may be identified with the strong INS band in the vicinity of 165–168 cm^{-1} because of the large amplitude of this motion. This motion is shown schematically in Figure 10. The intensity of this band did not show a strong orientational dependence because this motion possess both in-plane and out-of-plane components. It is interesting to note that the torsion of the complexed NH$_3$ occurs at a lower frequency than the corresponding one (R_z) from the uncomplexed NH$_3$ as mentioned above. This can be explained by the competition between NH$_3$–cation and NH$_3$–host interactions. As the attraction between the NH$_3$ and its neighboring cation becomes stronger, the hydrogen bonding between NH$_3$ and the host sulfur atoms weakens so that less energy is required to overcome the hydrogen–host attraction which hinders the NH$_3$ rotations about the

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[22] Lautie, A.; Novak, A. *Chem. Phys. Lett.* **1980**, *71*, 290.

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3-fold axis. This explanation is supported by the shift in band frequency as the cation is changed. Its frequency was observed at 165 ± 2, 167 ± 2, and 168 ± 2 cm^{-1} in the Ca^{2+}, Sr^{2+}, and Ba^{2+} compounds, respectively. The uncomplexed NH_3 does not experience this competition, and therefore its hydrogen bonding to the host is much stronger.

The bands in the ranges of 191–193 and 245–249 cm^{-1} are tentatively assigned to the symmetric metal–nitrogen stretching (ν_1) mode and asymmetric metal–nitrogen stretching (ν_3) mode, respectively, as illustrated in Figure 9. The intensities of both bands are enhanced when the incident beam is aligned parallel to the host basal plane as expected for in-plane stretching of the metal–NH_3 bond.

The rocking mode, $\varrho(NH_3)$, for complexed NH_3 is assigned to the intense, broad bands that are located in the regions 435–470, 410–460, and 405–425 cm^{-1} for the Ca^{2+}, Sr^{2+}, and Ba^{2+} compounds, respectively. This rocking motion is shown schematically in Figure 10. The reason for the structure in these bands lies most likely in the presence of complexes with different coordination numbers for which the frequencies of $\varrho(NH_3)$ will differ. These complexes may be formed and transformed as a result of the translational diffusion of NH_3 molecules between vacant metal coordination sites. Such behavior is consistent with the average coordination number of three determined from TGA. The magnitudes of the splittings in the INS bands for $\varrho(NH_3)$ of 10–30 cm^{-1} are consistent with differences in the binding energy of complexes with different coordination numbers estimated on the basis of ion–dipole and dipole–dipole interactions to be approximately 10^{-2} kcal/mol.

The assignment of $\varrho(NH_3)$ to the bands at 470 ± 6 and 435 ± 6 cm^{-1} in the calcium intercalate was confirmed by the INS experiments on oriented calcium–ammonia intercalates. These bands were more intense when the neutron beam was perpendicular to the host basal plane. A strong anisotropy of the vibrational bands in the INS spectra of the complexed NH_3 is expected on the basis of the anisotropic interaction imposed by the two-dimensional TiS_2 host.[6,7]

The systematic shift of $\varrho(NH_3)$ to lower values as the cation "size" is increased is consistent with the expectation that the stronger electrostatic field of Ca^{2+} causes a more severe local compression of its neighboring trigonal prismatic sites than Ba^{2+}. With the compression of the distance perpendicular to the basal plane, rocking of the NH_3 ligand would require more energy.

It is instructive to compare the rocking-mode frequency of the alkaline earth–ammonia complexes in TiS_2 with those of other known metal–ammine complexes. For NH_3 in $[KNH_3]^+Cl^-$ in an Ar matrix an IR band at[26,27] 460 cm^{-1} was assigned to $\varrho(NH_3)$, which is very close to that of complexed NH_3 in TiS_2. In transition-metal complexes $M(NH_3)_6$ or $M(NH_3)_4$ values for $\varrho(NH_3)$ typically range from 600 to 900 cm^{-1}.[25] Similarly, values for $\nu_{as}(M-N)$ for these complexes are in the range 400–500 cm^{-1} compared with approximately 245 cm^{-1} in the intercalated alkaline earth–ammonia complexes. This clearly shows that the metal–ammonia interactions of the intercalated complexes are relatively weak compared to those of transition-metal complexes. Ammonia interacts with the d orbitals of the metals in the transition metal complexes, whereas the alkaline earth–ammonia interaction is mainly of the ion–dipole type. The formation of solvation complexes in these systems depends strongly on a delicate balance between a complicated array of guest–host and guest–guest interactions. In ammoniated and alkali–ammoniated TiS_2 hydrogen bonding between NH_3 and the sulfide lattice competes with the attraction between the alkali cation and NH_3. Only for cations with a sufficiently large charge-to-radius ratio, such as lithium, the alkaline earth cations and ytterbium, can the cation–solvent attractions overcome the solvent–host interactions. This phenomenon can be demonstrated by comparing TiS_2 and graphite hosts. Lithium is the only alkali metal that forms stable complexes with NH_3 in TiS_2,[7,9] whereas in graphite both potassium and cesium are known[28] to form complexes with NH_3. However, weakly bound complexes of alkali cations (Li^+, Na^+, and Rb^+) with NH_3 have been identified in TiS_2 by INS experiments.[29]

The third species present in the alkaline earth–ammonia TiS_2 compounds is NH_4^+, which is formed by a redox reaction between TiS_2 and NH_3. However, no band in the region down to about 100 cm^{-1} in the INS spectra of these compounds could be assigned unambiguously to the NH_4^+ torsion, which normally is readily identified by its high INS intensity. This behavior is similar to that observed[10] previously for $(NH_3)_{0.36}(NH_4^+)_{0.20}TiS_2^{0.20-}$. However, in the partially deintercalated compound $(NH_4^+)_{0.20}TiS_2^{0.20-}$ the torsional mode of the NH_4^+ was easily identified at 215 cm^{-1}. The barrier to rotation for NH_4^+ in the latter compound was found by NMR experiments to be roughly 2–3 kcal/mol[9] which is in good agreement with the value of 2.4 kcal/mol estimated from the INS torsional frequency. It is possible that the rotation of the NH_4^+ ion in the presence of NH_3 is much less hindered than in its absence which could shift the torsional mode to a frequency below the range of the present INS experiments. This shift can be explained by the action of neighboring NH_3 molecules in propping the host slabs apart, which would weaken the guest–host interaction between TiS_2 and NH_4^+ and allow NH_4^+ ion to rotate more freely. Another possible explanation is that the ammonium ion develops a small dipole moment along one of the 3-fold N–H axes oriented parallel to the TiS_2 basal planes under these circumstances, as it does as an impurity in alkali halide crystals.[30] The observed dipole moment in NH_4^+ in these crystals is thought[30] to arise from either the fact that three of the H atoms on NH_4^+ are facing neighboring highly polarizable halide ions whereas the fourth H does not, or from the mismatch of the molecular (tetrahedral) and site symmetry (octahedral) which could result in an off-center

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[26] Nakamoto, K *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 4th ed.; John Wiley and Sons: New York, 1986, p 193.

[27] Loutellier, A.; Manceron, L.; Perchard, J. P. *Chem. Phys.* **1990**, *146*, 179–193.

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[29] Ong, E. W.; Eckert, J.; Burr, G.; Young, Jr., V. G.; Glaunsinger, W. S., manuscript in preparation.

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location for the center of mass of NH_4^+. If this were the case for NH_4^+ between the layers of TiS_2, its torsional mode would be predominantly about one 3-fold axis as it is for NH_3 and thus would not be distinguishable from the torsion of the latter. Such behavior could also result in the formation of NH_3–NH_4^+ complexes similar to those found in N_2H_7I, which have very different vibrational modes.[31,32] Recent NMR[9] and quasi-elastic neutron-scattering (QENS)[33] studies indicate that NH_4^+ ions in these systems execute rapid rotational motions even at very low temperatures and therefore support the hypothesis of a low barrier to rotation for this species.

The above results are consistent with the presence of molecular species within TiS_2 but are inconsistent with the dissociated–ammonia hypothesis proposed recently.[5] This model assumes that NH_3 within the TiS_2 intercalates exists as nonmolecular species consisting of nitrogen residing in crystallographic sites surrounded by protons which diffuse and tunnel very rapidly between interstitial sites in the TiS_2 vdW gaps. Although it is probable that protons exchange among the ammonia species in these compounds, our data indicate that the NH_3 behaves like molecular species, i.e., that the rate of this exchange is much slower than the rotational and vibrational frequencies of the molecules. Moreover, the INS vibrational spectra for hydrogen in metals[34] (Ti) and in several MS_2 systems[18] are well characterized and do not, in general, show any vibrational modes for terminal or interstitial hydrogen at frequencies below about 500 cm^{-1}. We believe therefore that the INS bands observed in this study are of molecular origin.

Conclusions

The combined data from TGA, DSC, XPS, evolved-gas pressure, and mass spectrometry experiments indicate the coexistence of two different NH_3 species as well as metal and NH_4^+ cations. The proportion of each species was found to be strongly dependent on the metal cation content within the intercalates. The different types of molecules were found to be energetically distinguishable by DSC and INS and to have different deintercalation enthalpies and different types of vibrational motions.

The results of this study lead to the following simplified picture of these materials. The guest species within the alkaline earth–ammonia intercalates behave as a solution trapped between host slabs, with NH_4^+ and alkaline earth cations as solutes surrounded by NH_3 molecules as the solvent. The NH_3 molecules within these compounds experience a competition between NH_3–H_4^+, NH_3–cation, and NH_3–host interactions. A delicate balance of these forces results in the coexistence of two different NH_3 species. Ammonia molecules that are closest to a metal cation may coordinate to it, while those farther away are more loosely bound and have greater motional freedom within the vdW gaps. The metal cations are surrounded by a well-defined solvation shell consisting of 2–6 NH_3 molecules. The complexed NH_3 shows internal vibrational modes of typical metal–ammine complexes. The NH_4^+ appears to be moving rapidly, probably by rotational diffusion, even at low temperatures. It is also probable that proton exchange between NH_4^+ and neighboring NH_3 molecules or host sulfur may occur. The rate and mechanism of this exchange will be the subject of a future publication.

A number of issues still need to be investigated. The strength of guest–guest interactions is strongly dependent on that of guest–host interactions. The calcium–ammonia intercalates of zirconium disulfide, tantalum disulfide, and molybdenum disulfide are currently being studied to examine this dependence. Furthermore, the lability of the complexed NH_3 from the alkaline earth–ammonia complex is at present unknown. An exchange experiment involving $^{14}NH_3$ and $^{15}NH_3$ molecules in calcium–ammonia and barium–ammonia TiS_2 intercalates is underway to measure the lability. A number of vibrational bands have not yet been assigned, as illustrated by Table 1. Possible coupling interactions between ligand and framework vibrational modes could give rise to these bands. Results from normal coordinate analysis computations and molecular dynamics simulations performed on the alkali–ammonia and alkaline earth–ammonia complexes using INS and QENS will be reported in a future paper.

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