give partial conversion (ca. 40%) of the carboxylic acid groups to acyl chlorides.

We have found that $Zr(O_3PCH_2CH_2COCl)_2$ can be easily converted to other novel layered materials in quantitative yields. Pure-phase amide and ester derivatives have been formed in this fashion. This chemistry will be the subject of an upcoming article.

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Existence of Metal–Ammonia Solvation Complexes in Lamellar Titanium Disulfide

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The relatively weak forces binding the layers of the lamellar transition metal disulfides (TS_2) make them logical choices for the investigation of solvation chemistry in two dimensions. A wide variety of solvated-cation intercalation compounds of these materials have been investigated.[1-4] However, the basic understanding of these systems has been limited by the paucity of information concerning guest–guest and guest–host interactions and the local arrangement of guest species. Sufficiently strong guest–guest interactions may lead to the formation of discrete solvation complexes between the layers of these materials. Herein, we report the first evidence for intercalated metal–ammonia solvation complexes for divalent and trivalent metals. Discrete solvent-to-metal coordination numbers of two, three, and possibly six, as well as coordination transitions, have been identified by thermal analysis of TiS_2 intercalation compounds.

Aqueous solvated-cation TS_2 intercalates can adopt both monolayer and bilayer forms, with fully hydrated compounds attaining bilayer and monolayer structures for solvated-cation charge-to-radius ratios of >1 and <1, respectively.[3,5] The dependence of the structure on the equilibrium water partial pressure and cation-exchange illustrates the structural importance of intercalant ion–dipole interactions.[3-5] Structural investigations to date have not revealed the presence of discrete solvation complexes but have indicated the general intercalant site coordination for selected intercalates.[6-11] Recent stability studies and complete structural refinement of the monolayer compound $(^7Li^+)_{0.22}(ND_3)_{0.63}TiS_2^{0.22-}$ using neutron powder diffraction (NPD) data illustrate for the first time the presence of discrete, monovalent $Li^+(ND_3)_3$ complexes between the TiS_2 layers.[12]

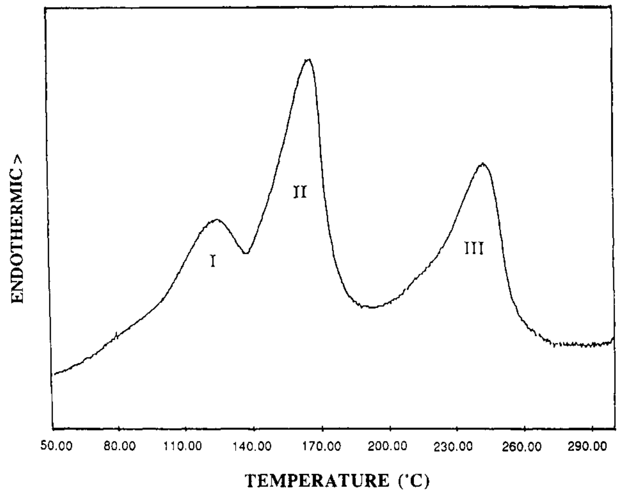

Figure 1. DSC of strontium–ammoniated TiS_2 intercalate showing the three endothermic peaks corresponding to the progressive deintercalation of NH_3^w (I), NH_3^s (II), and NH_4^+ (III).

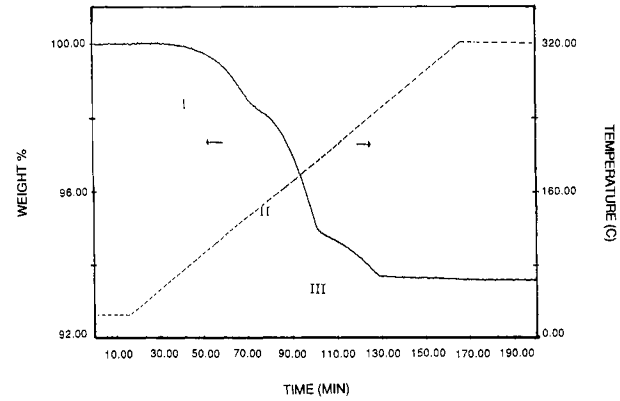

Figure 2. TGA of $(NH_4^+)_{0.09}[Ca^{2+}{}_{0.077}(NH_3^s)_{0.25}](NH_3^w)_{0.12}TiS_2^{0.24-}$ showing the three steps corresponding to the deintercalation of NH_3^w (I), NH_3^s (II), and NH_4^+ (III). Steps I and II are generally more clearly resolved for the higher charge density metal cations.

Highly stoichiometric TiS_2 ($Ti_{1.002}S_2$) was used as the host material.[13] Both the intercalates and the host were prepared, handled, and investigated under rigorous inert-atmosphere conditions.[14,15] Both the metal (M) and NH_3 undergo redox reactions during the intercalation process, with NH_3 forming NH_4^+, which intercalates more slowly than M.[15] These compounds exhibit charge compensation, with NH_4^+ intercalation continuing until the total charge transferred to the TiS_2 conduction band is about 0.23 mol of e^-/mol of TiS_2.[15] Hence, they are best described as $M_x^{n+}(NH_4^+)_{y'}(NH_3)_yTiS_2^{(nx+y')-}$, where nx +

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$y' = 0.23 \pm 0.02$ for $nx \leq 0.23$. This phenomena generally applies to metal–ammonia TiS_2 intercalates prepared by the liquid-ammonia technique.[15-19] Thermal deintercalation routinely results in successive ammonia and ammonium deintercalation, with complete thermal deintercalation of ammonia/ammonium being judged by the deintercalation of $y'NH_4^+$. The absence of deintercalation during further heating as well as X-ray powder diffraction confirm the formation of $M_x^{n+}TiS_2^{nx-}$.[2,15,17]

The deintercalation energetics and quantities of the volatile species in the Ca, Sr, and Yb intercalates were determined by using differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). As illustrated in Figures 1 and 2, deintercalation occurs in three distinct steps for $y' > 0$. Vapor pressure measurements coupled with mass spectrometric evolved-gas analysis of the deintercalation process indicate only NH_3 is liberated in the first two steps, whereas a 2:1 mole ratio of NH_3 and H_2 is evolved in the third.[16] The third step is due to ammonium loss, while the first two steps demonstrate the presence of weakly and strongly bound NH_3. Thus, the deintercalation process proceeds in the following sequence:

$$(NH_4^+)_{y'}[M_x^{n+}(NH_3^s)_{y''}](NH_3^w)_{y'''}TiS_2^{(nx+y')-} \xrightarrow[-y'''NH_3]{} \quad (I)$$

$$(NH_4^+)_{y'}[M_x^{n+}(NH_3^s)_{y''}]TiS_2^{(nx+y')-} \xrightarrow[-y''NH_3]{} \quad (II)$$

$$(NH_4^+)_{y'}M_x^{n+}TiS_2^{(nx+y')-} \xrightarrow[-[y'NH_3 + (y'/2)H_2]]{} M_x^{n+}TiS_2^{nx-} \quad (III)$$

where NH_3^s and NH_3^w represent strongly and weakly bound NH_3, respectively. Distinct NH_3 and NH_4^+ peaks were observed by X-ray photoelectron spectroscopy, which shows that these chemical species coexist within these compounds and are not artifacts of thermal treatment.

The low- and intermediate-temperature DSC endotherms in Figure 1 correspond to the deintercalation of NH_3^w and NH_3^s having deintercalation enthalpies (ΔH_D) of 13 ± 2 and 19 ± 2 kcal/mol of NH_3, respectively. As anticipated, $\Delta H_D(NH_3^s) > \Delta H_D(NH_3^w)$, and $\Delta H_D(NH_3^s)$ is approximately twice that reported for $(NH_4^+)_{y'}(NH_3)_yTiS_2^{y'-}$ (10.5 kcal/mol of NH_3).[20] The high-temperature endotherm reflects NH_4^+ deintercalation. The observed enthalpy is the same within experimental error as that previously observed for $(NH_4^+)_{y'}(NH_3)_yTiS_2^{y'}$ (22 kcal/mol of NH_4^+).[20] These enthalpies represent the total energy required to remove each species from the host and include contributions from hydrogen bonding, M–NH_3 bond cleavage, electrostatic and elastic lattice energies, and desorption. A detailed study of the energetics of these compounds is in progress.

The dependence of the NH_3^s concentration (y'') on M is displayed in Figure 3 for M = Ca, Sr, and Yb. The existence of discrete y''/x ratios that are independent of x over a range of x indicates that NH_3^s is actually complexed with M. This means that y''/x can be interpreted as the coordination number of the metal in regions where y''/x is constant. Therefore, these intercalates are best described as containing NH_4^+, M–NH_3 complexes, and should result in stronger ion–dipole and ion–induced dipole attractions between M and NH_3, which may lead to M–uncomplexed NH_3 as the intercalated species. Complex formation occurs both in the presence and absence of NH_4^+. The higher charge density of M^{n+} relative to NH_4^+ NH_3 complex formation.

The coordination numbers of these complexes are a function of the M^{n+} charge (q) and size (r), as shown in Figure 3 and Table I, with higher values of q/r favoring lower coordination numbers. The Sr, and possibly also the

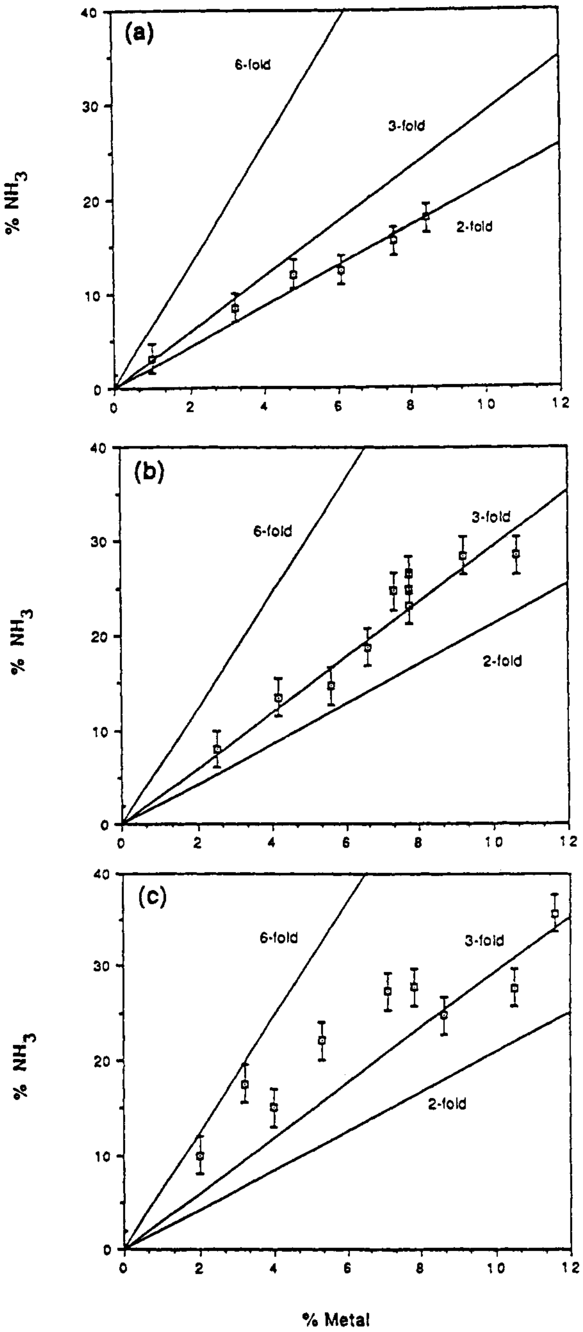

Figure 3. Mole percent $NH_3^s(y'')$ vs mole percent $M^{n+}(x)$ for $M^{n+} = Yb^{3+}$ (a), Ca^{2+} (b), and Sr^{2+} (c).

Table I. Solvated Complex Coordination Numbers (y''/x) as a Function of Metal (M^{n+}) and Concentration (x) for Intercalated $M_x^{n+}(NH_3)_{y''}$ Complexes

M^{n+}	x	y''/x
Sr^{2+}	$0.00 < x < 0.03$	6
Sr^{2+}	$0.03 \leq x \leq 0.08$	6 → 3
Sr^{2+}	$0.08 \leq x \leq 0.12$	3
Ca^{2+}	$0.00 \leq x \leq 0.10$	3
Yb^{3+}	$0.00 < x < 0.05$	3 → 2
Yb^{3+}	$0.06 \leq x \leq 0.09$	2

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Yb, intercalates exhibit gradual coordination transitions with increasing x from 6-fold to 3-fold and from 3-fold to 2-fold, respectively. At low metal concentrations, the complexes are probably discrete units, in which case a mixture of 6- and 3-fold complexes or 3- and 2-fold complexes may coexist in the transition region for the Sr–NH$_3$ and Yb–NH$_3$ compounds, respectively. The complex behavior for Sr may be related to the "softness" of the large Sr^{2+} ion, which results in a poorer definition of its solvation sphere. The rather poor resolution of NH$_3^s$ and NH$_3^w$ for Ba–NH$_3$ compounds supports this view. Such coordination number transitions underscore the delicate balance between the guest–guest and guest–host interactions in these materials.

The Ca and Sr intercalates in this study are stage I, monolayer compounds having a 3R-type structure. The cell constants of the intercalates are in the range a = 3.421 ± 0.003 Å and c = 26.2 ± 0.06 Å over the entire concentration range examined, with no systematic variations. The resulting 3.04 ± 0.02 Å occupied-layer expansion (OLE) is less than previously observed for $(ND_4^+)_{0.22}(ND_3)_{0.34}TiS_2^{0.22-}$,[21] where ammonia is responsible for the observed OLE of 3.21 Å. However, it is significantly greater than the OLE range observed for stage II $(NH_4^+)_{y'}TiS_2^{y'-}$ (2.54–2.85 Å),[22] indicating NH$_3$ is still responsible for the observed OLEs for these intercalates. The independence of the OLE from NH$_4^+$ concentration lends further support to this conclusion. Consequently, these 6-, 3-, and 2-fold solvated complexes are two-dimensional in nature. The observed two-dimensional coordination numbers fit very well with hexagonal host–layer symmetry and trigonal–prismatic guest sites. The XPD intensities are similar to those observed for ammoniated and lithium–ammoniated TiS$_2$ intercalates,[15,21] indicating similar layer structures with trigonal prismatic guest sites for these intercalates. Combined XPD and NPD investigations for selected compounds are in progress.

In summary, we have found that (1) Yb, Ca, Sr, and Ba form two-dimensional solvation complexes with NH$_3$ in TiS$_2$, (2) higher values of metal ion q/r prefer lower coordination numbers, (3) these complexes exhibit coordination number transitions as a function of metal concentration, and (4) the solvation numbers are strongly influenced by the symmetry of the host. The definition of the solvation sphere for Ba^{2+} in these compounds is rather poor, although the presence of NH$_3^s$ could be detected by DSC. Attempts to study the strong complexation expected for Mg–NH$_3$ compounds has not been successful to date due to the low solubility of Mg in NH$_3$. Furthermore, preliminary results indicate that Ca also forms two-dimensional solvation complexes with NH$_3$ between the layers of NbS$_2$, which suggests that the formation of such two-dimensional solvated complexes may indeed be a general phenomenon.

A full account of our work on the existence of metal–ammonia solvation complexes in lamellar transition metal disulfides will be published in the near future.

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Nonlinear Optical Characteristics of Novel Inorganic Chromophores Using the Zindo Formalism

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The search for molecules possessing large second-order optical nonlinearities (i.e., having large β values) is currently an area of intense activity.[1–6] Once identified, such molecules can be incorporated into macroscopic assemblies to form materials exhibiting very large nonlinear optical (NLO) responses. To date, experimental and theoretical efforts have focused primarily on π-conjugated *organic* chromophores, particularly those with electron-withdrawing and electron-accepting substituents linked through an intervening π-backbone.[1–6] As exploratory synthetic efforts expand to include chromophores containing main-group and transition-metal constituents, the need arises for accurate, computationally efficient, and chemically oriented quantum chemical approaches to describing the nonlinear optical properties of such chromophores.

There are several theoretical approaches for calculating molecular nonlinear optical responses. Computationally intensive methods such as coupled Hartree–Fock,[7] derivative Hartree–Fock,[8] correlated wave[9] ab initio, and finite field[7a,9,10] procedures are currently applicable only to molecules of limited size. More elaborate chromophores are generally treated within a perturbative framework where the electronic states created by the laser field are expressed as a sum over unperturbed excited particle–hole states.[7a,11] Since the NLO expansion coefficients are functions of linear optical properties such as excitation energies and dipole matrix elements, the electronic structure models of choice are spectroscopically based semiempirical algorithms. Indeed, previous sum over states (SOS) studies have employed either a modified all-valence CNDO/S[12–15] or a π-electron PPP (Parr–Par-

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