Chem. Mater. 1991, 3, 14-17

Table II. Fe/Co Ratio of Thin Films Prepared by PCVD Using $Fe(CO)_5/Co(CO)_3NO$ and $Fe(CO)_5/Co_2(CO)_8$ Precursors at Different Vaporization Temperatures[a]

T, °C			
$Fe(CO)_5$ (°C)	$Co(CO)_3NO$ (°C)	$Co_2(CO)_8$ (°C)	Fe/Co ratio
20	-1		1.40
20	4		1.25
20	20		1.00
2	20		0.78
20		45	0.66
5		45	0.21
0		45	0.13

[a] These results represent the average values of at least two different films, and the margin of error was ±10%.

Therefore, PCVD experiments using a 345-nm long-pass filter to selectively excite this M → π*NO absorption band of $Co(CO)_3NO$ should yield Co-rich films relative to control experiments using no filter. On the contrary, if a 325-nm bandpass filter is used such that the percent transmittance at 374 nm is reduced to ~0.1, Fe-rich films should be obtained. The results in Table I demonstrate that the relative proportions of Fe and Co in alloy thin films, as determined by XRF, can be manipulated in a predictable fashion using this selective excitation approach. The only published report on wavelength control of film composition was by Armstrong et al.,[10] in which two different Fe/Ni ratios were obtained by using metallocene precursors and two different lasers as irradiation source. Under their experimental conditions, "significant carbon content" was found in the resulting films,[10] compared with the <1% C found in our Fe–Co films (see below).

The Fe/Co ration in the deposited films can also be controlled in a systematic manner by the vaporization temperatures and hence the vapor pressures of the metal carbonyl precursors. By simply varying the vaporization temperatures of the precursors, both Fe- and Co-rich films can be prepared, as shown in Table II. Therefore, this PCVD technique allows the fine control of film compositions and could lead to thin films with interesting electrical or magnetic properties.

The Fe–Co thin films prepared by PCVD were examined by Auger electron spectroscopy (AES), and a typical depth profile analysis is shown in Figure 2. Our results indicate that Fe and Co are uniformly distributed throughout the thickness of the film and that 5–10% O and <1% C are present. It is believed that most of bulk oxide in the deposited film arises from background gases during deposition and could probably be eliminated by using lower deposition pressures in an improved apparatus. Electrical conductivity measurement of the above Fe–Co film using the four-point probe technique gave a resistivity of 34.4 μΩ cm. The saturation magnetization, σ_{sat}, of the same Fe–Co film was 24.2 emu/g, as measured by a vibrating sample magnetometer (VSM) operating at 10 kOe. This translates to a saturation moment, μ_{sat}, of 0.50 μ_3/atom, which is substantially lower than the theoretical value of 2.3 μ_3/atom predicted by the Slater–Pauling curves[11] for a 1:1 Fe–Co thin film. The lower saturation moment is probably due to the presence of antiferromagnetic iron and cobalt oxides in these films, as suggested by Auger analysis results. A detailed investigation of the magnetic properties of PCVD-derived Fe–Co thin films as a function of film compositions is underway.

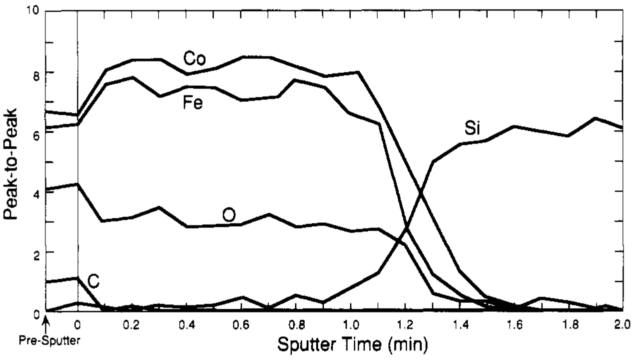

Figure 2. Auger depth profile of Fe–Co film deposited on Si substrate by PCVD using $Fe(CO)_5$ and $Co(CO)_3NO$ precursors at 20 °C. The sputtering rate was ~1000 Å/min using Ar^+ ions.

The mechanism for the thin film deposition via the photolysis of group VI (Cr, Mo, W) metal carbonyl precursors has been studied by Singmaster et al.[12] It was found that coordinatively unsaturated metal carbonyls formed via gas-phase photolysis can undergo further photochemical and/or thermal CO loss on the surface to form metallic thin films.[12] We believe a similar mechanism is responsible for the deposition of Fe–Co films from Fe and Co metal carbonyls in our experiments.

In summary, we have demonstrated that mixed-metal thin films can be deposited at ambient temperature via the photodecomposition of simple metal carbonyls and that the composition of such films may be controlled systematically by the excitation wavelength as well as the vaporization temperatures of the precursors.

Acknowledgment. We thank Mr. R. Giauque, Dr. K.-M. Yu, and Mr. M. Chandramouli for assistance with the XRF, XRD, and VSM measurements, respectively. This work was supported by the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

---

(9) Evans, W.; Zink, J. I. *J. Am. Chem. Soc.* **1981**, *103*, 2635.

(10) Armstrong, J. V.; Burk, A. A.; Coey, J. M. D.; Moorjani, K. *Appl. Phys. Lett.* **1987**, *50*, 1231.

(11) Morrish, A. H. *Physical Principles of Magnetism*; Wiley: New York, 1965.

(12) Singmaster, K. A.; Houle, F. A.; Wilson, R. J. *J. Phys. Chem.* **1990**, *94*, 6864.

Synthesis of Layered $Zr(O_3PCH_2CH_2COCl)_2$ from $Zr(O_3PCH_2CH_2COOH)_2$

David A. Burwell and Mark E. Thompson*

Frick Chemical Laboratory, Princeton University
Princeton, New Jersey 08544

Received October 10, 1990
Revised Manuscript Received November 26, 1990

Layered metal organophosphonates have received a great deal of attention in recent years due primarily to their use in materials design, ion exchange, and catalysis.[1]

---

(1) (a) Alberti, G. In *Recent Developments in Ion Exchange*; Williams, P. A., Hudson, M. J., Eds.; Elsevier Applied Science: New York, 1987. (b) Alberti, G.; Constantino, U. *J. Mol. Catal.* **1984**, *27*, 235–250. (c) Clearfield, A. In *Design of New Materials*; Cocke, D. L., Clearfield, A., Eds.; Plenum Press: New York, 1988. (d) Clearfield, A. *Chem. Rev.* **1988**, *88*, 125–148. (e) Johnson, J. W.; Brody, J. F.; Alexander, R. M.; Pilarski, B.; Katritzky, A. R. *Chem. Mater.* **1990**, *2*, 198–201. (f) Johnson, J. W.; Jacobson, A. J.; Butler, W. M.; Rosenthal, S. E.; Brody, J. F.; Lewandowski, J. T. *J. Am. Chem. Soc.* **1989**, *111*, 381–383. (g) Lee, H.; Kepley, L. J.; Hong, H.; Mallouk, T. E. *J. Am. Chem. Soc.* **1988**, *110*, 618–620.

0897-4756/91/2803-0014$02.50/0

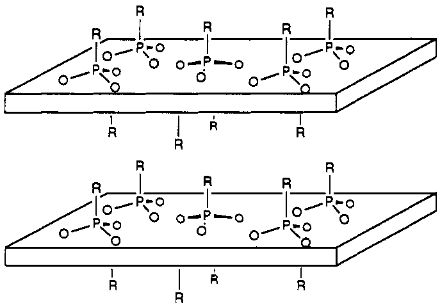

Figure 1. Schematic drawing of layered metal phosphonate.

These materials are intercalation hosts that contain alternating organic and inorganic layers.[2] They were first synthesized by Alberti et al. in 1978 and were soon after expanded on by Dines and co-workers.[3,4] Group 4 metal phosphonates ($M(O_3PR)_2 \cdot nH_2O$) generally have the same layered structure as α-$Zr(O_3POH)_2 \cdot H_2O$ (α-ZrP).[2a] Each layer consists of a plane of metal atoms linked by phosphonate groups (Figure 1). The metal atoms are octahedrally coordinated by oxygen atoms, with the three oxygens of each phosphonate tetrahedron bound to three different metal atoms. This arrangement forces the organic groups to lie above and below the inorganic layer. $Zr(O_3PCH_2CH_2COOH)_2$ is one such layered solid that readily intercalates n-alkylamines or ammonia in a Brønsted acid/base reaction, yielding $Zr(O_3PCH_2CH_2COO^-)_2(RNH_3^+)_2$.[5] Apart from this reaction, however, no other organic chemistry has been reported for layered group 4 metal phosphonates. In this paper we report the conversion of $Zr(O_3PCH_2CH_2COOH)_2$ to $Zr(O_3PCH_2CH_2COCl)_2$. The new acyl chloride retains the layered structure of the carboxylic acid. This synthesis extends the range of useful intercalation reactions for layered metal phosphonates and opens the door for the preparation of previously unobtainable layered compounds via the reactive acyl chloride.

$Zr(O_3PCH_2CH_2COOH)_2$ was prepared according to the literature procedure of Dines and DiGiacomo.[4a] It has an interlayer spacing (12.9 Å) and ^{13}C NMR and IR spectra consistent with interlayer hydrogen bonding between carboxylic acid groups, as proposed by Környei and Szirtes.[6] Attempts to directly convert $Zr(O_3PCH_2CH_2COOH)_2$ to $Zr(O_3PCH_2CH_2COCl)_2$ by treating the solid carboxylic acid with thionyl chloride, oxalyl chloride, and phosphorus pentachloride failed.[7] In no instance was there any indication of reaction in the interlayer region as determined by powder X-ray diffraction (XRD) and IR. If, on the other hand, the layered carboxylic acid was "preintercalated" with ammonia and then treated with thionyl chloride, the acyl chloride could be formed quantitatively. It appears that the interlayer dimerlike bonding of the acid groups physically blocks reaction of the chlorinating agents with the host's interior by presenting only very narrow channels for guest molecule intercalation. Alternatively, the interlayer hydrogen bonding may thermodynamically prohibit the direct conversion of the acid to the acyl chloride. In either case, preintercalation of ammonia facilitates the chlorination step since it increases the interlayer spacing by 2.4 Å and, presumably, disrupts the interlayer hydrogen-bonding network.

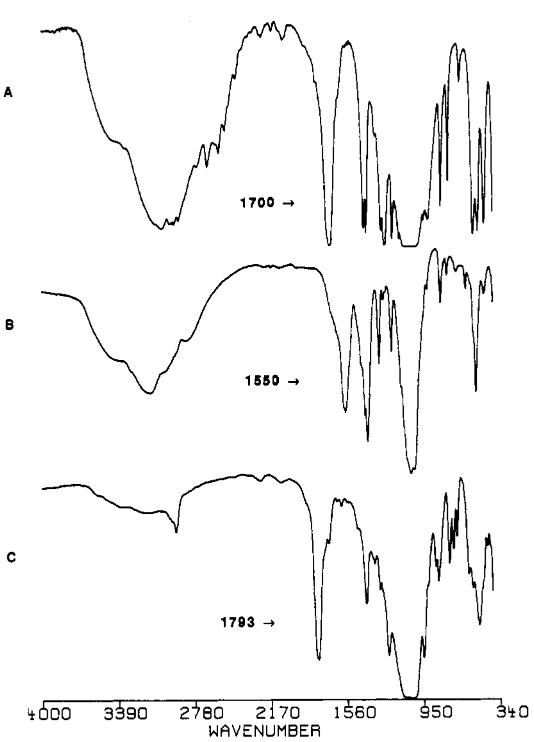

Figure 2. FTIR spectra of (A) $Zr(O_3PCH_2CH_2COOH)_2$, (B) $Zr(O_3PCH_2CH_2COO^-)_2(NH_4^+)_2$, and (C) $Zr(O_3PCH_2CH_2COCl)_2$.

Preintercalation has also been employed in the reaction of α-ZrP with ethylene oxide[8] and in ion-exchange reactions.[9] Several years ago, Yamanaka found that the γ-phase of zirconium phosphate (γ-ZrP) with an interlayer spacing of 12.2 Å reacted with ethylene oxide to form $Zr(O_3POCH_2CH_2OH)_x(O_3POH)_{2-x} \cdot H_2O$ derivatives.[10] The more crystalline α-ZrP with an interlayer spacing of 7.6 Å did not, however, react in a similar fashion. It was proposed that the smaller interlayer spacing of α-ZrP prevented diffusion of ethylene oxide through the interlayer region and, therefore, limited reaction to the surface of the solid. Later, Clearfield found that if α-ZrP was pre-intercalated or "swelled" with butylamine, ethylene oxide could diffuse into the interior of the solid and react completely with α-ZrP.[8]

The ammonium intercalate, $Zr(O_3PCH_2CH_2COO^-)_2(NH_4^+)_2$, was prepared by passing anhydrous ammonia

---

(2) (a) Alberti, G.; Constantino, U. In *Intercalation Chemistry*; Whittingham, M. S., Jacobson, A. J., Eds.; Academic Press: New York, 1982. (b) Ortiz-Avila, C. Y.; Rudolf, P. R.; Clearfield, A. *Inorg. Chem.* **1989**, *28*, 2137–2141. (c) Clearfield, A. *Comm. Inorg. Chem.* **1990**, *10*, 89–128. (d) Johnson, J. W.; Jacobson, A. J.; Brody, J. F.; Lewandowski, J. T. *Inorg. Chem.* **1984**, *23*, 3842–3844. (e) Cao, G.; Lee, H.; Lynch, V. M.; Mallouk, T. E. *Solid State Ionics* **1988**, *26*, 63–69. (f) Cao, G.; Lee, H.; Lynch, V. M.; Mallouk, T. E. *Inorg. Chem.* **1988**, *27*, 2781–2785. (g) Cao, G.; Lynch, V. M.; Swinnea, J. S.; Mallouk, T. E. *Inorg. Chem.* **1990**, *29*, 2112–2117.

(3) Alberti, G.; Constantino, U.; Allulli, S.; Tomassini, N. *J. Inorg. Nucl. Chem.* **1978**, *40*, 1113–1117.

(4) (a) Dines, M. B.; DiGiacomo, P. M. *Inorg. Chem.* **1981**, *20*, 92–97. (b) Dines, M. B.; Griffith, P. C. *Polyhedron* **1983**, *2*, 607–611. (c) Dines, M. B.; Griffith, P. C. *Inorg. Chem.* **1983**, *22*, 567–569. (d) Dines, M. B.; Cooksey, R. E.; Griffith, P. C.; Lane, R. H. *Inorg. Chem.* **1983**, *22*, 1004–1006.

(5) Környei, J.; Szirtes, L.; Constantino, U. *J. Radioanal. Nucl. Chem.* **1985**, *89/2*, 331–338.

(6) Környei, J.; Szirtes, L. *J. Radioanal. Nucl. Chem.* **1984**, *83/2*, 257–260.

(7) Reactions with thionyl chloride and oxalyl chloride were carried out in neat refluxing liquids and in common organic solvents (e.g., pyridine, methylene chloride, toluene, dimethylformamide) at temperatures ranging from 0 to 150 °C. Reactions with phosphorus pentachloride were performed in xylenes up to a temperature of 140 °C.

(8) Ortiz-Avila, C. Y.; Clearfield, A. *Inorg. Chem.* **1985**, *24*, 1773–1778.

(9) Constantino, U. *Chem. Soc., Dalton Trans.* **1979**, 402–405.

(10) Yamanaka, S. *Inorg. Chem.* **1976**, *15*, 2811–2817.

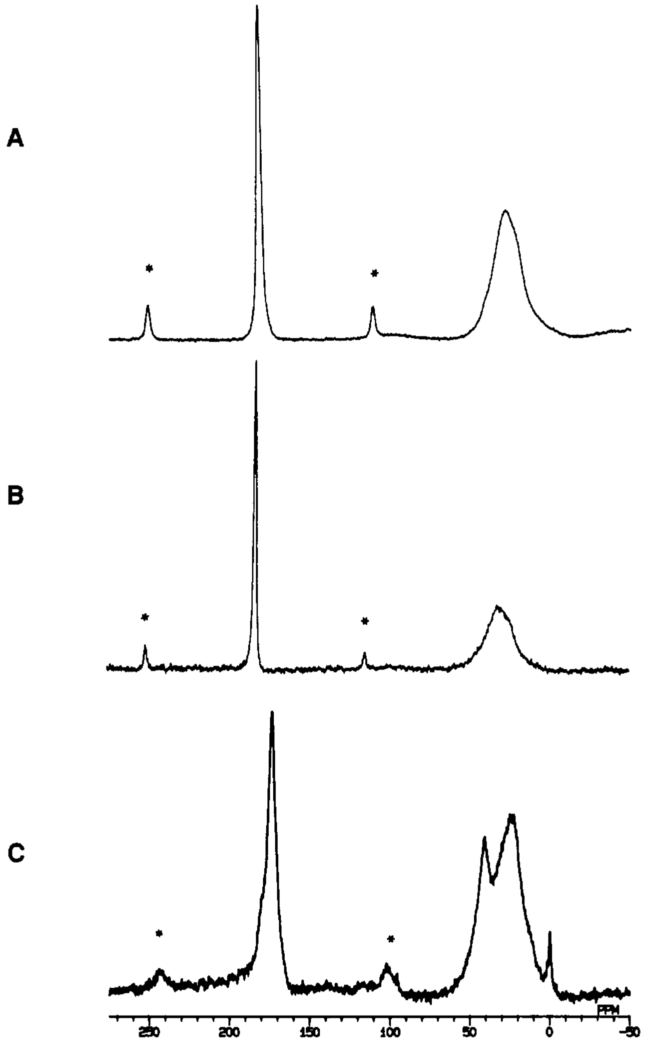

Figure 3. ^{13}C CP MAS NMR spectra of (A) $Zr(O_3PCH_2CH_2COOH)_2$, (B) $Zr(O_3PCH_2CH_2COO^-)_2(NH_4^+)_2$, and (C) $Zr(O_3PCH_2CH_2COCl)_2$ at 67.9 MHz; asterisks denote spinning sidebands.

(National/Bower) through a round-bottom flask containing solid $Zr(O_3PCH_2CH_2COOH)_2$, eq 1.

$$Zr(O_3PCH_2CH_2COOH)_2 \xrightarrow{NH_3(g)} Zr(O_3PCH_2CH_2COO^-)_2(NH_4^+)_2 \quad (1)$$

$$Zr(O_3PCH_2CH_2COO^-)_2(NH_4^+)_2 \xrightarrow[\text{neat, reflux}]{SOCl_2} Zr(O_3PCH_2CH_2COCl)_2 \quad (2)$$

$Zr(O_3PCH_2CH_2COO^-)_2(NH_4^+)_2$ (5 g) was then added in small portions (ca. 0.5 g) to a flask containing 100 mL thionyl chloride (Aldrich, 99+%) cooled to 0 °C under a nitrogen purge. The flask was placed in a 90 °C oil bath, where the mixture was stirred until the reaction was complete, eq 2. The thionyl chloride was then removed and the solid product dried under vacuum. Although some surface reaction occurred on contact, reaction in the interlayer region took place relatively slowly—requiring 2 weeks in refluxing thionyl chloride to fully convert the carboxylate salt to the acyl chloride. Interestingly, at no point in the reaction was there evidence for acid anhydride formation, as determined by IR and powder XRD.[11]

Characterization of the product by IR and ^{13}C and ^{31}P solid-state NMR spectroscopies and powder XRD indicated quantitative conversion of the carboxylate to the acyl chloride. The ν_{CO} shifted from 1700 to 1550 to 1793 cm^{-1} as the compound was converted from carboxylic acid to carboxylate salt to acyl chloride (Figure 2). The carboxyl ^{13}C isotropic shift changed from 180.9 to 183.0 to 173.7 ppm for this same sequence (Figure 3).[12] The methylene regions of the ^{13}C spectra contain very broad resonances. Apparently, magic angle sample spinning does not completely average the chemical shift of each methylene to one isotropic signal. This is presumably due to some type of static disorder, such as a dispersion of local environments for a given methylene. Investigations are currently underway to determine the exact nature of this signal broadness. The ^{31}P isotropic shift moved from 12.4 to 8.0 to 5.5 ppm.[13] Powder XRD patterns showed an increase in interlayer spacing from 12.9 to 15.3 Å upon intercalation of ammonia, followed by a decrease to 13.5 Å after treatment with thionyl chloride. The powder XRD pattern of $Zr(O_3PCH_2CH_2COCl)_2$ exhibited three orders of 0*k*0 reflections. The reflections were slightly broadened and decreased in intensity relative to $Zr(O_3PCH_2CH_2COOH)._2$

$Zr(O_3PCH_2CH_2COCl)_2$ was found to be air stable for short periods of time; however, prolonged exposure to moisture resulted in reformation of $Zr(O_3PCH_2CH_2COOH)_2$. It was also found that the yield of acyl chloride suffered if the synthesis was not carried out according to the described addition sequence. That is, if the addition order was reversed and 0 °C thionyl chloride was added to the carboxylate salt, the acyl chloride yield was reduced to ca. 50%.

The layered acyl chloride was also prepared in lower yields from the butylammonium, octylammonium, cesium ion, and lithium ion carboxylate salts of $Zr(O_3PCH_2CH_2COOH)_2$ by reaction with thionyl chloride. The ammonium intercalate was chosen for the general synthesis due to its ease of use and consistently high yields. No salt of $Zr(O_3PCH_2CH_2COO^-)_2$ reacted with oxalyl chloride or phosphorus pentachloride. Finally, it should be noted that the acyl chloride cannot be prepared directly from $ZrOCl_2{\cdot}8H_2O$ by treatment with $(HO)_2P(O)CH_2CH_2COCl$. While the phosphonic acid can be made, the reaction conditions required to prepare the zirconium phosphonate would lead to further reaction at the acyl carbon.

We have been less successful at converting other members of the layered carboxylic acid zirconium phosphonate family (i.e., $Zr(O_3P(CH_2)_nCOOH)_2$) to acyl chlorides. Results to date indicate that $Zr(O_3PCH_2COOH)_2$ and $Zr(O_3PCH_2CH_2CH_2COOH)_2$ can be partially converted to the corresponding acyl chlorides; however, pure-phase materials have not been prepared. Other recent work may suggest an attractive alternative to preintercalation for weakening interlayer bonding in carboxylic acid terminated zirconium phosphonates. Thionyl chloride has been found to react directly with mixed-component zirconium phosphonate–phosphate $Zr(O_3PCH_2CH_2COOH)_x(O_3POH)_{2-x}{\cdot}nH_2O$ and phosphonate–phosphite $Zr(O_3PCH_2CH_2COOH)_y(O_3PH)_{2-y}{\cdot}mH_2O$ compounds[14] to

---

[11] Acid anhydride formation might be expected from the reaction of an acyl chloride with an adjacent carboxylic acid group.

[12] ^{13}C NMR spectra were recorded on a JEOL 270 spectrometer (67.9 MHz) equipped with a 7.5-mm multinuclear MAS probe from Chemagnetics, Inc. High-power ^1H decoupling, cross polarization (CP), and magic angle spinning (MAS) were employed. Signals are relative to TMS by using adamantane as a secondary external reference.

[13] ^{31}P NMR spectra were recorded on a JEOL 270 spectrometer (109 MHz) equipped with a 7.5-mm multinuclear MAS probe from Chemagnetics, Inc. High-power ^1H decoupling and MAS were employed. Signals are relative to 85 wt % H_3PO_4 used as an external reference.

[14] TGA suggests that $x \approx 1.5$ and $y \approx 1$ for our compounds. (a) Alberti, G.; Constantino, U.; Környei, J.; Giovagnotti, L. *React. Polym.* **1985**, *4*, 1–10. (b) Alberti, G.; Constantino, U.; Marmottini, F. In *Recent Developments in Ion Exchange*; Williams, P. A., Hudson, M. J., Eds.; Elsevier Applied Science: New York, 1987.

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.

Acknowledgment is made to the donors of the Petroleum Research Foundation, administered by the American Chemical Society, and to the Air Force Office of Scientific Research (AFOSR-90-0122) for the support of this project.

Existence of Metal–Ammonia Solvation Complexes in Lamellar Titanium Disulfide

E. W. Ong, M. J. McKelvy, L. A. Dotson, and W. S. Glaunsinger*

Department of Chemistry and
Center for Solid State Science
Arizona State University
Tempe, Arizona 85287-1604

Received May 25, 1990
Revised Manuscript Received November 19, 1990

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]

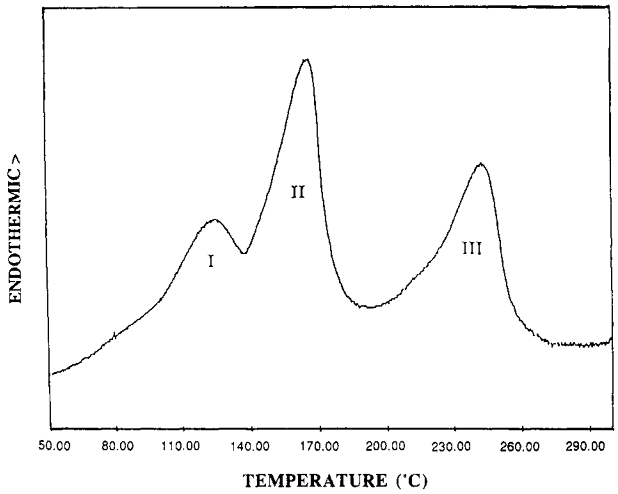

Figure 1. DSC of strontium–ammoniated TiS_2 intercalate showing the three endothermic peaks corresponding to the progressive deintercalation of NH_3^w (I), NH_3^s (II), and NH_4^+ (III).

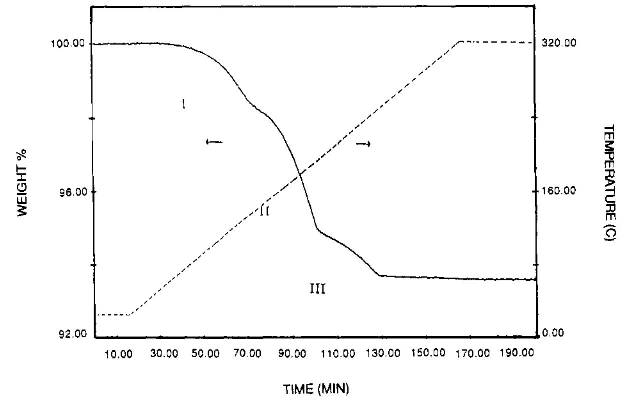

Figure 2. TGA of $(NH_4^+)_{0.09}[Ca^{2+}_{0.077}(NH_3^s)_{0.25}](NH_3^w)_{0.12}TiS_2^{0.24-}$ showing the three steps corresponding to the deintercalation of NH_3^w (I), NH_3^s (II), and NH_4^+ (III). Steps I and II are generally more clearly resolved for the higher charge density metal cations.

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 +

---

[1] Subba Rao, G. V.; Shafer, M. W. *Intercalated Layered Materials*; D. Reidel: Dordrecht, Holland, 1979; pp 99–199.

[2] Rouxel, J. *Intercalated Layered Materials*; D. Reidel: Dordrecht, Holland, 1979; pp 201–250.

[3] Schöllhorn, R. *Intercalation Chemistry*; Academic Press: New York, 1982; pp 315–374.

[4] Schöllhorn, R. *Inclusion Compounds*; Academic Press: London, 1984; pp 249–349.

[5] Lerf, A.; Schöllhorn, R. *Inorg. Chem.* **1977**, *16*, 2950–2956.

[6] Schöllhorn, R.; Weiss, A. *Z. Naturforsch.* **1973**, *28b*, 711–715.

[7] Wiegers, G. A.; van der Meer, R.; van Heiningen, H.; Kloosterboer, H. J.; Alberink, A. J. A. *Mater. Res. Bull.* **1974**, *9*, 1261–1266.

[8] Whittingham, M. S. *Mater. Res. Bull.* **1974**, *9*, 1681–1690.

[9] Graf, H.; Lerf, A.; Schöllhorn, R. *J. Less-Common Met.* **1977**, *55*, 213–220.

[10] Bos-Alberink, A. J. A.; Haange, R. J.; Wiegers, G. A. *J. Less-Common Met.* **1979**, *63*, 69–80.

[11] Patel, S. N.; Balchin, A. A. *J. Mater. Sci.* **1985**, *20*, 917–921.

[12] Young, Jr., V. G.; McKelvy, M. J.; Glaunsinger, W. S.; Von Dreele, R. B. *Chem. Mater.* **1990**, *2*, 75–81.

[13] McKelvy, M. J.; Glaunsinger, W. S. *J. Solid State Chem.* **1987**, *66*, 181–188.

[14] Bernard, L.; McKelvy, M.; Glaunsinger, W.; Colombet, P. *Solid State Ionics* **1985**, *15*, 301–310.

[15] McKelvy, M.; Bernard, L.; Glaunsinger, W.; Colombet, P. J. *Solid State Chem.* **1986**, *65*, 79–88.

0897-4756/91/2803-0017$02.50/0