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Intercalation of Pyridine into the Layered SmSI Structure of YbOCl

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The SmSI structure type of YbOCl (hexagonal, a = 3.726 (1) Å, c = 27.830 (5) Å) can be intercalated at room temperature with dried pyridine (py) to give the intercalation compound, $(py)_{0.1}YbOCl$. The presence of H_2O in the pyridine leads to the formation of pyH^+ and the resulting compound, $(H_2O)_{0.7}[(py)_{0.129-x}(pyH^+)_x]YbOCl$. Deintercalation of the pyridine occurs at 120 °C, whereas that of the pyH^+ occurs at 290 °C. The X-ray powder diffraction pattern for either compound can be indexed as a 3R structure type with a = 3.7020 (3) Å and c = 42.79 (2) Å. The increase in the interlayer separation of 4.99 Å indicates that the plane of the pyridine molecule is oriented perpendicular to the layers of YbOCl. Intercalation of 4-ethylpyridine shows an increase in the interlayer separation of ~7 Å, indicating that the lone pair on the nitrogen and the plane of the molecule is oriented perpendicular to the layers. Infrared spectroscopy supports the conclusion that there is coordination of pyridine to the YbOCl host through the nitrogen. The intercalation reaction is described as an acid-base reaction.

Introduction

The interest in studying intercalation compounds of various materials is motivated by the unique properties that these materials possess. These properties range from anisotropic electron transport[1] to superconductivity[2] and more recently to spontaneous magnetization.[3] Several of these materials have been employed in energy storage materials, electrochromic displays, and catalysis.[4] The intercalation chemistry of the transition metal dichalogenides, graphite, and the layered oxide bronzes has been studied the most intensely[5] with new host materials such as the transition-metal phosphorus trisulfides attracting recent interest.[6]

The driving force for intercalation into layered materials depends upon both the electronic and structural features of the host. Experiments have shown that intercalation of Lewis bases into transition-metal dichalcogenides is accompanied by a guest-host redox reaction.[7] For these hosts, it has been shown that there exists partially filled bands that can accept electron density from the guest intercalate.[7] In many cases, the upper limit of intercalation (i.e., the maximum amount of the guest species that can be intercalated) is determined by the energy associated with the filling of these bands. In other host systems, such as the layered oxides, it has been shown that intercalation of Lewis bases into these materials is better described as an acid-base reaction.[8]

Although there are large numbers of layered transition-metal compounds whose intercalation chemistry has been explored,[9] there are relatively few examples of low-temperature intercalation of lanthanide layered compounds.[10,11] Lithium and sodium insertion compounds of the three-dimensional rare-earth compounds, UO_3 and U_3O_8, have been reported and are of interest as potential cathodic materials.[12] The lanthanide metal oxychlorides, LnOCl (Ln = Ho, Er, Tm, and Yb), can be prepared as layered structures, and there is evidence that low-temperature intercalation of these structures by alkali metals is possible.[10] We recently reported the intercalation of sodium and ammonia into YbOCl.[11]

During our investigation of the sodium intercalates of YbOCl via the liquid ammonia route, we noted that ammonia easily intercalates into YbOCl.[13] We were interested in investigating pyridine as a Lewis base intercalate since pyridine intercalation reactions in transition metal layered materials have been widely studied[14] and $(py)_xYbOCl$ would be the first example of a lanthanide pyridine intercalation compound. We have intercalated pyridine and 4-ethylpyridine into YbOCl and describe the synthesis, structural characterization, thermogravimetric analysis (TGA), and infrared spectroscopy (IR) of these compounds.

Experimental Section

Synthesis. *YbOCl*, crystallizing in the SmSI structure type, is obtained by the low-temperature methods described by Garcia et al.[10] Briefly, Yb_2O_3 (Research Chemicals, 99.999%) is reacted with NH_4Cl in a 20% molar excess at 300 °C in a quartz boat to form $(NH_4)_3YbCl_6$. Upon completion of the reaction (indicated by cessation of NH_3 evolution), H_2O saturated Ar is slowly passed

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(1) Gamble, F. R.; Geballe, T. H. In *Treastise on Solid State Chemistry*; Hanny, N. B., Ed.; Plenum Press: New York, 1976; Vol. III, pp 106-166.

(2) (a) Formstone, C. A.; Fitzgerald, E. F.; O'Hare, D.; Cox, P. A.; Kurmoo, M.; Hodby, J. W.; Lillicrap, D. Goss-Custard, M. *J. Chem. Soc., Chem. Commun.* **1990**, 501. (b) Tanuma, S.; Iye, Y.; Koike, Y. In *Physics of Intercalation Compounds*; Pietronero, L., Tosatti, E.; Eds. Springer-Verlag: Berlin, 1981; Solid State Sciences, Vol. 38, p 298. (c) Gamble, F. R.; Osiecki, J. H.; Cais, M.; Pisharody, R.; Di Salvo, F. J.; Geballe, T. H. *Science* **1971**, *174*, 493. (d) Gamble, F. R.; DiSalvo, F. J.; Klemm, R. A.; Geballe, T. H. *Science* **1970**, *168*, 568. (e) Gamble, F. R.; Thompson, A. H. *Solid State Commun.* **1978**, *27*, 379.

(3) Clement, R.; Lomas, L.; Audiere, J. P. *Chem. Mater.* **1990**, *2*, 641.

(4) (a) Harris, S.; Chianelli, R. R. *Chem. Phys. Lett.* **1983**, *101*, 603. (b) Weisser, O.; Landa, S. *Sulfide Catalysts: Their Properties and Applications*; Pergamon Press: Oxford, U.K., 1973. (c) Whittingham, M. S.; Ebert, L. B. In *Intercalated Layered Materials*; Levy, F. A., Ed.; D. Riedel: Dordrecht, Holland, 1979; Vol. 6, pp 533-562. (d) Smith, J. J. *Naval Res. Rev.* **1985**, *2*, 3.

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

(6) Brec, R. In *Review on Structural and Chemical Properties of Transition Metal Phosphorus Trisulfides MPS_3*; Dresselhaus, M. S., Ed.; *Intercalation in Layered Materials*; NATO ASI Series B; Plenum Press: New York, 1986; Physics Vol. 148, pp 93-124.

(7) McKelvy, M. J.; Glausinger, W. S. *Solid State Ionics* **1987**, *25*, 287.

(8) Schöllhorn, R.; Nolle-Schulte, T.; Steinhoff, G. *J. Less Common Met.* **1980**, *71*, 71.

(9) (a) *Intercalation in Layered Materials*; Dresselhaus, M. S., Ed., Plenum Press: New York, 1987; Vol. 148, NATO Series B. (b) Rouxel, J. *Chem. Scr.* **1988**, *28*, 33. (c) Rouxel, J. *J. Chim. Phys.* **1986**, *83*, 841.

(10) Garcia, E.; Corbett, J. D.; Ford, J. E.; Vary, W. J. *Inorg. Chem.* **1985**, *24*, 494.

(11) Odink, D.; Kauzlarich, S. M. *Mol. Cryst. Liq. Cryst.* **1990**, *181*, 325.

(12) Dickens, P.; Powell, A. V.; Chippindale, A. M. *Solid State Ionics* **1988**, *28-30*, 1123.

(13) Odink, D. A.; Kauzlarich, S. M., unpublished research.

(14) *Pyridine-Metal Complexes*; Neskome, G. R., Strekowski, L., Eds.; *The Chemistry of Heterocyclic Compounds*; John Wiley & Sons: New York, 1985; Chapter 6.

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over the solid to form YbOCl (R$\bar{3}$m-type (a mix of YOF + SmSI structure types)) in quantitative yield. The R$\bar{3}$m composite mix was dried under vacuum at 250 °C for a minimum of 3 h and then transferred to an inert-atmosphere drybox. The sample was then mixed in a molar ratio of 10:1 KCl–LiCl flux:YbOCl, sealed under vacuum in a silica ampule, and heated at 450 °C for 2 weeks to obtain predominantly the SmSI structure type. LiCl was sublimed under vacuum, and KCl was dried at 500 °C under vacuum. The flux was separated from the YbOCl by multiple washings with distilled H_2O and finally with methanol. On the basis of X-ray powder diffraction techniques, the SmSI phase of YbOCl obtained in this manner is approximately 90% pure, with the remaining 10% being the YOF structure type. The product was characterized by X-ray powder diffraction, thermogravimetric analysis, and infrared spectroscopy.

Pyridine (py) (Fischer, Certified A.C.S.) and 4-ethylpyridine (Aldrich Chemicals) were stored over KOH pellets, distilled onto CaO, and then distilled once more to remove H_2O. The pyridines were degassed three times prior to transferring via syringe to a flask containing YbOCl. A second reaction employing only degassed pyridine was performed to evaluate the effect of water on the reaction.

$(py)_x$YbOCl. This intercalation compound was obtained by stirring 200 mg of YbOCl in 25–30 mL of pyridine for a period of 5–30 days at room temperature. Pyridine was removed via cannula, and the resulting solid was dried for 1 h under vacuum. In duplicate experiments, the solid was washed with degassed absolute ethanol, prior to drying under vacuum, in order to remove pyridine adsorbed on the surface. There were no discernible differences between the material washed with ethanol and the material dried under vacuum. Intercalation of the host was confirmed by X-ray powder diffraction (in most cases approximately 5–10% of unintercalated YbOCl remain). For reactions containing water (present in the pyridine), a stoichiometric value of $x = 0.129$ was obtained for the pyridine. Analytical data (in wt %) for $(H_2O)_{0.7}(py)_{0.129}YbOCl$ found (calculated): C 3.14% (3.13%), N 0.76% (0.73%), H 0.82% (0.83%).[15] The TGA data show a total weight loss of about 8%, less than the expected ~9% weight loss, although the TGA curve never flattens out. The lower than expected weight loss in the TGA may be due to the formation of HCl gas which occurs when the sample decomposes to form Yb_2O_3. Some of the H in the analysis may also be due to a small amount of YbOOH impurity, although none was observed by X-ray powder diffraction. The IR spectrum shows peaks at 1625 and 600–750 cm-1, characteristic of H_2O and consistent with the interpretation that there is water either co-intercalated or adsorbed on the sample. For reactions involving no water (rigorously dried, distilled pyridine), a value of $x = 0.10$ is calculated from TGA data. The final product is hygroscopic, and care was taken to ensure minimal exposure to air or water.

(4-ethyl-py)$_x$YbOCl was prepared in the manner described above. No reactions were attempted to investigate the effects of H_2O. It was notably more difficult to intercalate 4-ethylpyridine as reaction times of 2 weeks at room temperature provided samples with approximately 50% of the sample intercalated, as determined from X-ray powder diffraction.

Characterization. All samples were characterized by X-ray powder diffraction using a focusing Guinier camera (Enraf-Nonius) equipped with a silica monochromator to give Cu Kα_1 radiation. NBS silicon was included as an internal standard, the five lines being fit to known diffraction angles by a nonlinear least-squares function. The samples were mounted between pieces of transparent tape (samples were handled under inert atmosphere conditions, however, the pyridine intercalates do not appear to be oxygen sensitive). The powder camera was then evacuated (10^{-4} Torr) in order to maintain sample integrity. A Siemens D-500 powder diffractometer (Cu Kα radiation) was used to obtain peak profiles for several samples. Spectra were taken at 0.02°/s over the 2θ range of 7–85°.

Nuclear magnetic resonance (^{1}H), infrared and UV–vis spectra were taken of the pyridine solutions prior to, during, and after the intercalation reactions. There are no differences detected in these spectra, indicating that YbOCl does not decompose in this solvent to form a soluble species such as a pyridine–ytterbium chloride complex. However, in the pyridine solutions isolated from the externally heated reactions several small red needle crystals were observed after evaporation of the solvent. The crystals were not of X-ray quality and not in sufficient yield to characterize by optical spectroscopy. Several pyridine–ytterbium complexes have been characterized,[16] and it is suspected that these needles are a pyridine–ytterbium complex indicating that there is a small amount of decomposition of the sample upon heating.

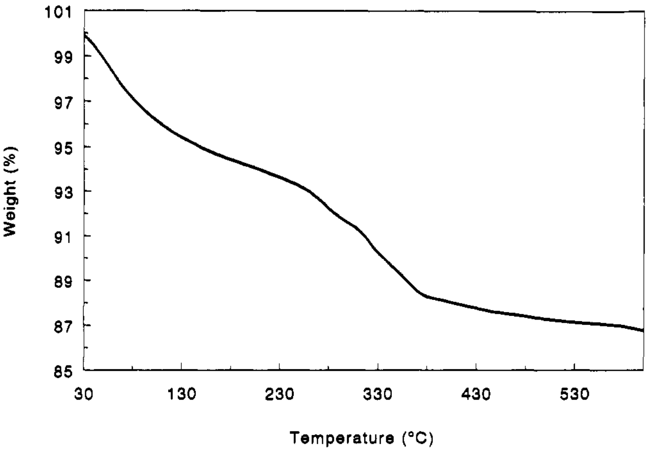

Figure 1. Thermogravimetric analysis curve of YbOCl, dried in vacuo and handled in air.

IR data were obtained from powder samples ground and pressed into KBr pellets on an IR/32 IBM spectrometer. UV-vis spectra were obtained on a Hitachi U-2000 spectrophotometer. Powders were ground into mulls with mineral oil. A du Pont System 951 thermogravimetric analyzer was used for the TGA experiments. The microbalance on the thermogravimetric unit was calibrated before each experiment. The samples (~10–20 mg) were heated at 2 °C/min from 35 to 600 °C under a continuous flow (50 cm^3/min) of argon. The sample, $(H_2O)_{0.7}(py)_{0.129}YbOCl$ was heated at 2 °C/min from 70 to 510 °C under a continuous flow of argon. In some cases, the evolved gas was trapped at −78 °C and subsequently analyzed with a Finnegan MAT GC/MS.

Results and Discussion

Synthesis. YbOCl (SmSI structure type) could be synthesized in high yield according to the literature preparation. Although YbOCl is not O_2 sensitive, it is very hygroscopic. It was necessary to dry the YbOCl at 250 °C for a minimum of 3 h under high vacuum (10^{-6} Torr) to remove all traces of water, as determined by zero weight loss in the TGA. Figure 1 shows the TGA data for YbOCl that has been dried in vacuo and handled in air. There are two distinct weight losses indicating two different water interactions. The first corresponds to water absorbed on the surface of the powder, while the second is a result of water bound more tightly. There are no differences in the X-ray diffraction patterns of the wet and dried (250 °C, 10^{-6} Torr drying) samples implying that the H_2O molecules are not within the van der Waals gap. The TGA were taken from 35 to 600 °C. At about 600 °C the sample begins to decompose with the evolution of HCl and the formation of Yb_2O_3. Mass spectral analysis of the gases evolved during thermal treatment to 300 °C confirms that water is the only species present. If there is any H_2O present in either YbOCl or the LiCl/KCl flux, then small amounts of silicates can be observed by X-ray powder diffraction in the final product. Therefore care was taken to ensure that all the materials used were thoroughly dried prior to the flux reaction.

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(15) Berkeley Microanalytical Laboratory, University of California, Berkeley, CA 94720.

(16) (a) Wayda, A. L.; Mukerji, I.; Dye, J. L. *Organometallics* **1987**, *6*, 1328. (b) Thomas, A. C. Ph.D. Dissertation, University of Wisconsin, Madison, WI, 1986.

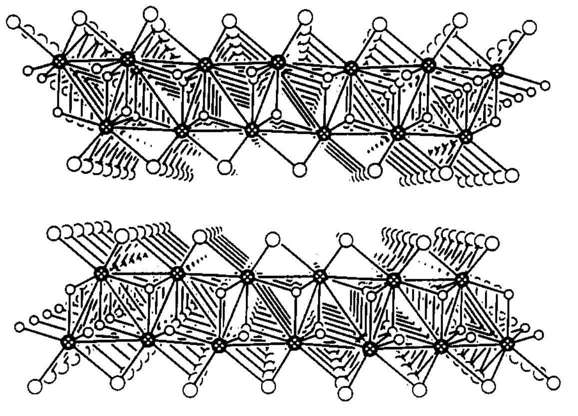

Figure 2. Two layers of the YbOCl (SmSI structure-type). Chlorine, oxygen, and ytterbium atoms are denoted by large open, small open, and cross-hatched circles, respectively.

Pyridine can be successfully intercalated into YbOCl to give the composition $(py)_{0.10}YbOCl$. To evaluate the nature of this reaction, various conditions were employed in the synthesis of the intercalation compound. Reactions extending for periods of up to 1 month showed little increase in the value of pyridine intercalated. Water present during the reaction lead to a stoichiometry of $(H_2O)_{0.7}(py)_{0.129}YbOCl$. The water present in the reaction produced pyH^+ and the composition of the intercalate can be more accurately identified as $(H_2O)_{0.7}[(py)_{0.129-x}(pyH^+)_x]YbOCl$ based on TGA and IR data which are discussed below. There is no evidence for 4,4′-bipyridine in either sample, determined from IR and MS data. Since the amount of pyridine is far below that of which would be theoretically possible based on a hard-sphere model (0.75), the reaction flask was externally heated to ~70 °C for several days. The products isolated from these reactions are faint blue, and the X-ray powder diffraction showed very little intercalated product. A similar result was obtained for pyridine intercalation into TmOCl.[13] Optical spectra of these products show a steady increase in absorbance from the near IR to the visible region with no maxima. The interpretation of this behavior is uncertain, but since the spectra for the pyridine intercalates show no absorbance over the same region, particle size effects can be ruled out.

Structure. The layered structure (SmSI or YOF structure-type) of YbOCl consists of two hexagonally packed ytterbium layers sandwiched between layers of chlorine with oxygen atoms filling the tetrahedral holes between Yb layers. The chlorine atoms line the edges of the van der Waals gap. The structure of these slabs is shown in Figure 2. The unit cell for either structure type, SmSI or YOF, contains three of these slabs and occurs in the space group, $R\bar{3}m$. Figure 3 shows the [110] projection of the SmSI structure type where the layers are sequenced ABC; in the YOF structure type, the slabs are sequenced ACB. A powder pattern of YbOCl was calculated[17] using single-crystal data[18] and gives excellent agreement with YbOCl (SmSI structure-type) obtained by this low-temperature method. YbOCl crystallizes in the hexagonal space group $R\bar{3}m$ with lattice constants a = 3.726 (1) Å, c = 27.830 (5) Å.

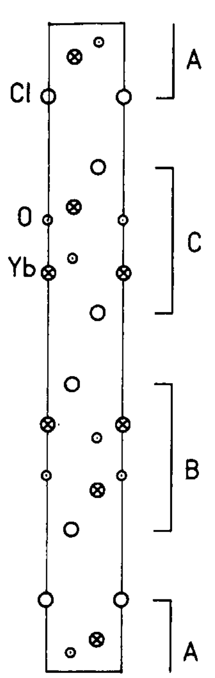

Figure 3. [110] projection of the SmSI structure-type. Each layer is outlined and identified as A, B, and C. Chlorine, oxygen, and ytterbium atoms are represented as open, dotted, and cross-hatched circles, respectively.

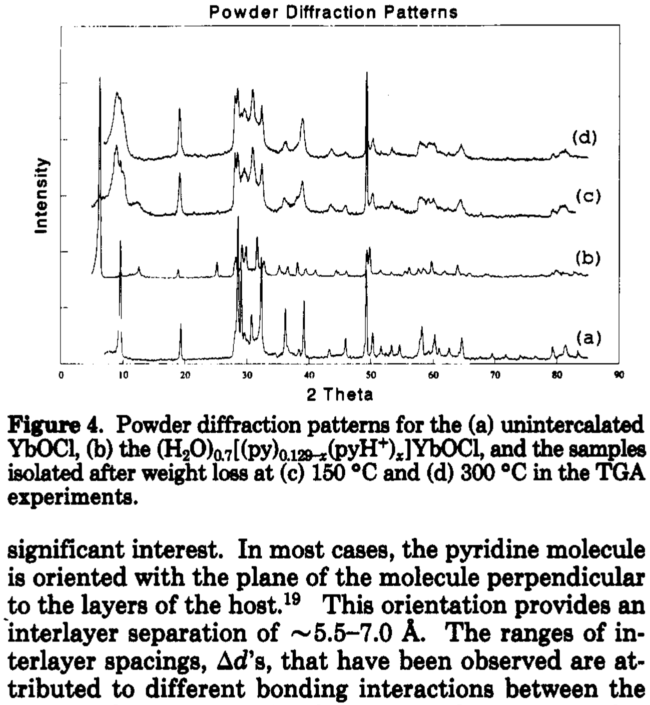

Figure 4. Powder diffraction patterns for the (a) unintercalated YbOCl, (b) the $(H_2O)_{0.7}[(py)_{0.129-x}(pyH^+)_x]YbOCl$, and the samples isolated after weight loss at (c) 150 °C and (d) 300 °C in the TGA experiments.

The orientation of the pyridine molecule within the van der Waals gap of layered materials has been a topic of significant interest. In most cases, the pyridine molecule is oriented with the plane of the molecule perpendicular to the layers of the host.[19] This orientation provides an interlayer separation of ~5.5–7.0 Å. The ranges of interlayer spacings, Δd's, that have been observed are attributed to different bonding interactions between the guest and host. For the dichalcogenides, neutron diffraction studies[20] as well as the intercalation of substituted pyridine molecules[19] show that the plane of the molecule is perpendicular and the lone-pair electrons on nitrogen are oriented parallel to the layers. A few intercalation compounds have been isolated in which the plane of the molecule is oriented parallel (Δd = 3.3 Å) to the layers of the host.[3,19] Structural models have been proposed for amine intercalates of FeOCl and other metal oxychlorides based on lattice expansions and Mössbauer,[21,22] NMR,[23]

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(17) Clark, C. M.; Smith, D. K.; Johnson, G. J. A Fortran IV Program for Calculating X-ray Powder Diffraction Patterns—Version 5; Department of Geosciences, The Pennsylvania State University: University Park, PA, 1973.

(18) Brandt, G.; Diehl, R. *Mater. Res. Bull.* **1974**, *9*, 411.

(19) Whittingham, M. S. *Mater. Res. Bull.* **1978**, *13*, 775.

(20) (a) Riekel, C.; Hohlwein, D.; Schöllhorn, R. *J. Chem. Soc., Chem. Commun.* **1976**, 863. (b) Riekel, C.; Fischer, C. O. *J. Solid State Chem.* **1979**, *29*, 181.

(21) Eckert, H.; Herber, R. H. *J. Chem. Phys.* **1984**, *80*, 4526.

Table I. Calculated[26] versus Observed X-ray Powder Diffraction Data for $(H_2O)_{0.7}[(py)_{0.129-x}(pyH^+)_x]YbOCl$. Lattice Parameters Obtained for Indexing on the Hexagonal 3*R* Cell Are *a* = 3.7020 (3) Å and *c* = 42.79 (2) Å

d_{expt}, Å	d_{calc}, Å	*hkl*	I_{obs}	I_{YOF}	I_{SmSI}
14.540	14.263	003	100	100	100
7.169	7.131	006	5	1	1
4.771	4.754	009	5	1	2
3.569	3.566	0012	10	2	2
3.197	3.197	101	10	0	3
3.169	3.171	012	15	5	0
3.069	3.071	104	20	0	10
3.002	3.002	015	20	11	1
2.853	2.853	0015	10	2	2
2.838	2.839	107	25	2	9
2.749	2.750	018	10	7	3
2.565	2.566	1010	5	5	1
2.472	2.474	0111	5	0	5
2.377	2.377	0018	10	2	2
2.298	2.297	1013	5	4	1
2.212	2.212	0114	5	1	3
2.087	2.054	1016	3	1	2
2.051	2.038	0021	3	1	1
1.980	1.980	0117	3	2	0
1.850	1.851	110	20	4	4
1.835	1.836	113	20	1	4
1.789	1.792	116	3	1	1
1.725	1.725	119	3	1	1
1.642	1.643	1112	3	2	2
1.602	1.602	021	5	0	1
1.598	1.598	202	5	1	0
1.585	1.585	024	5	0	2
1.575	1.576	205	5	2	1
1.551	1.553	027	5	1	2
1.535	1.536	208	10	1	1
1.500	1.501	0210	3	1	1
1.482	1.482	2011	3	0	1
1.460	1.460	1118	5	2	2
1.441	1.441	0213	3	1	0
1.210	1.210	122	3	1	0
1.204	1.204	214	3	0	2
1.200	1.200	125	3	2	1
1.189	1.189	217	3	1	2
1.182	1.182	128	3	2	1

and pseudo-single-crystal[24] studies. The currently accepted model for the transition metal oxychlorides is one in which the 2-fold axis of the pyridine molecule is oriented perpendicular to the layers.

Figure 4 shows the X-ray powder diffraction patterns of YbOCl, $(H_2O)_{0.7}[(py)_{0.129-x}(pyH^+)_x]YbOCl$, and the intercalate after heating at 150 and 300 °C. Upon intercalation of pyridine, the X-ray powder diffraction pattern shows an increase (Δd) of 4.99 Å in the basal spacing and the powder diffraction pattern can be indexed as a hexagonal 3*R* (three layers, rhombohedral) structure-type with $a = 3.7020$ (3) Å and $c = 42.79$ (2) Å. Table I shows the observed and calculated *d* spacings for the 3*R* structure-type for $(H_2O)_{0.7}[(py)_{0.129-x}(pyH^+)_x]YbOCl$ (from Guinier data) and the observed intensities. Table I also includes the calculated intensities for the SmSI[18] and YOF[25] structure, obtained by calculating the new positional parameters for the expanded structure and leaving the van der Waals gap empty.[26] Although the majority of scattering is due to the YbOCl layers, the calculated models do not provide enough differences in intensities to be able to assign the intercalated compound to either the SmSI or YOF structure. In addition, assigning structures based on intensities of several peaks is complicated by preferred orientation in layered materials.[10] It is possible that upon intercalation the resulting compound is a mixture of SmSI and YOF structure types. Powder patterns of $(H_2O)_{0.7}[(py)_{0.129-x}(pyH^+)_x]YbOCl$ and $(py)_{0.10}YbOCl$ are identical, and lattice parameters obtained for both stoichiometries are within experimental error. It is not possible to determine whether the H_2O is within the van der Waals gap based on the X-ray diffraction, IR spectroscopy, or TGA data. Since YbOCl is hygroscopic and the interlayer spacing is approximately the same for the intercalates, it is likely that the H_2O is simply adsorbed on the surface of the $(H_2O)_{0.7}[(py)_{0.129-x}(pyH^+)_x]YbOCl$ sample. The increase in interlayer spacing of 4.99 Å indicates that the plane of the pyridine molecule is oriented perpendicular to the plane of the YbOCl layers. To determine the relative orientation of the lone pair electrons on nitrogen with respect to the YbOCl layers, the intercalation of 4-ethylpyridine into YbOCl was investigated. This reaction is only about 50% complete after 2 weeks at room temperature, and it is not possible to obtain accurate *a* or *c* lattice parameters, but X-ray powder diffraction data show an increase in the interlayer spacing of ~7 Å. This is consistent with the lone-pair electrons on nitrogen and the plane of the molecule being oriented perpendicular to the YbOCl layers as indicated schematically in Figure 5.

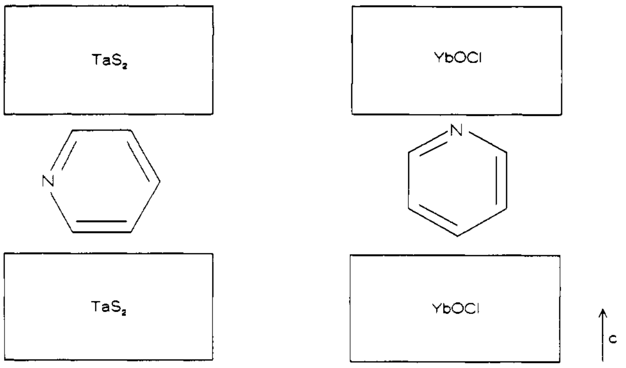

Figure 5. Orientation of pyridine molecules in TaS_2 and YbOCl.

IR Spectroscopy. Figure 6 shows the IR spectrum for $(H_2O)_{0.7}[(py)_{0.129-x}(pyH^+)_x]YbOCl$ and $(py)_{0.1}YbOCl$. Water is present in the IR for $(H_2O)_{0.7}[(py)_{0.129-x}(pyH^+)_x]YbOCl$ as seen by the broad absorption at 1625 and 600–750 cm^{-1}. The fact that these absorptions are broad may indicate that the H_2O is simply adsorbed on the surface. There are two fundamentals of YbOCl that occur between 650 and 400 cm^{-1}, and therefore pyridine modes in this range are not readily distinguished. Several vibrational modes of pyridine are sensitive to coordination of an acceptor and these bands shift to higher frequency upon complexation.[27]

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(22) (a) Kanamaru, F.; Shimada, M.; Koizumi, M.; Takano, M.; Takada, T. *J. Solid State Chem.* **1973**, *7*, 297. (b) Kikkawa, S.; Kanamaru, F.; Koizumi, M. *Physica* **1981**, *105B*, 249. (c) Kikkawa, S.; Kanamaru, F.; Moizumi, M. *Bull. Chem. Soc. Jpn.* **1979**, *52*, 963. (d) Maeda, Y.; Yamashita, M.; Ohshio, H.; Tsutsumi, N.; Takashima, Y. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 3138. (e) Herber, R. H. *Acc. Chem. Res.* **1982**, *15*, 216. (f) Herber, R. H.; Maeda, Y. *Inorg. Chem.* **1981**, *20*, 1409. (g) Fatseas, G. A.; Palvadeau, P.; Venien, J. P. In *Solid State Chemistry*; Proceedings of the 2nd European Congress, Veldhoven, The Netherlands, June 7–9, 1982. Metselaar, R., Heijligers, H. J. M., Schoonman, J., Eds. *Studies in Inorganic Chemistry*; Elsevier: Amsterdam, 1983; Vol. 3, pp 627–630. (h) Kanatzidis, M. G.; Tonge, L. M.; Marks, T. J.; Marcy, H. O.; Kannewurf, C. R. *J. Am. Chem. Soc.* **1987**, *109*, 3797.

(23) (a) Rouxel, J.; Palvadeau, P. *Rev. Chim. Min.* **1982**, *19*, 317. (b) Clough, S.; Palvadeau, P.; Venien, J. P. *J. Phys. C: Solid State Phys.* **1982**, *15*, 641.

(24) Parry, G. S.; Scruby, C. B.; Williams, P. M. *Philos. Mag.* **1974**, *29*, 601.

(25) Mann, A. W.; Bevan, D. J. N. *Acta Crystallogr., Sect. B* **1970**, *B26*, 2129.

(26) The calculated powder patterns were obtained by adjusting the reported *z* positional parameters so as to give the correct interatomic distances: SmSI (from ref 18): *z*(Yb) = 0.3664, *z*(Cl) = 0.0729, *z*(O) = 0.3126; YOF (from ref 25): *z*(Yb) = 0.1994, *z*(Cl) = 0.4278, *z*(O) = 0.1448.

(27) *Spectroscopy and Structures of Molecular Complexes*; Yarwood, J., Ed.; Plenum: New York, 1973; pp 150-1, 281-2, 359-60.

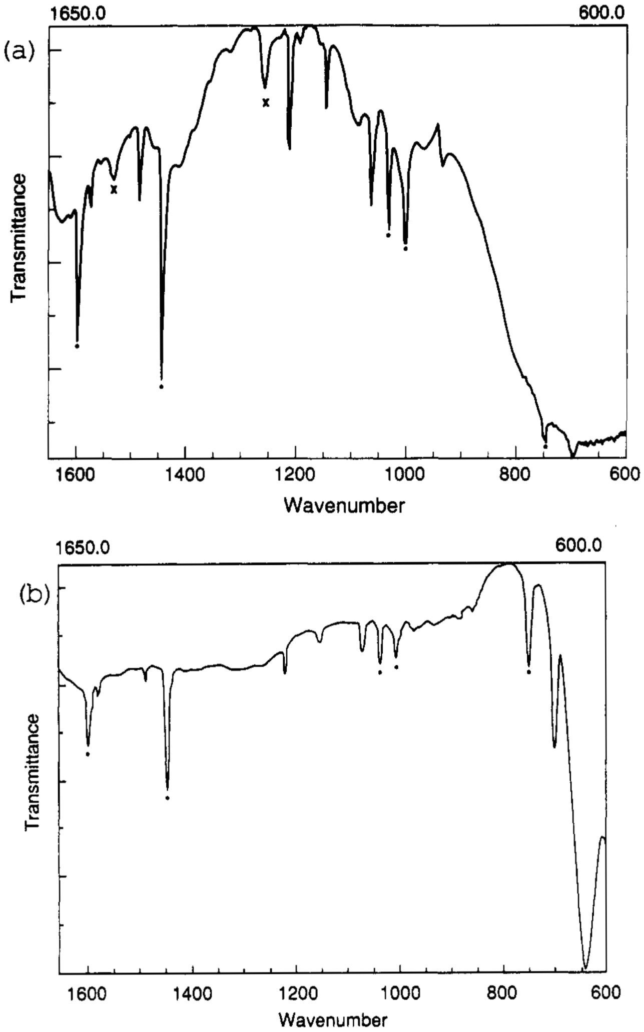

Figure 6. Infrared spectra of (a) $(H_2O)_{0.7}[(py)_{0.129-x}(pyH^+)_x]YbOCl$ and (b) $(py)_{0.1}YbOCl$. Peaks indicated with dots represent modes shifted to higher frequency upon complexation to an acceptor. Peaks indentified with crosses indicate the presence of pyridinium ions.

In free pyridine, these bands occur at 1599, 1439, 1029, 992, and 745 cm^{-1}. The IR spectrum shows that these bands, designated by ● in Figure 6, are shifted to 1596, 1443, 1035, 1005, and 748 cm^{-1}. The frequency shift of these modes is consistent with the pyridine molecule acting as a Lewis base and forming an adduct within the layers as presented in Figure 5. Before intercalation, the Yb is in a bicapped trigonal antiprismatic site, with a Cl from across the van der Waals gap as one of the capping atoms.[18] After intercalation, this site would be available for coordination by the lone pair on the nitrogen of pyridine so that Yb is acting as a Lewis acid site for the pyridine molecule, which is a Lewis base. In comparing the IR spectra for $(py)_{0.10}YbOCl$ and $(H_2O)_{0.7}[(py)_{0.129-x}(pyH^+)_x]YbOCl$ compounds, in addition to the peaks assigned to water, $(H_2O)_{0.7}[(py)_{0.129-x}(pyH^+)_x]YbOCl$ shows two additional absorption peaks indicated with an × in Figure 6. Although the frequency of the N–H^+ stretch in pyridinium occurs at 2439 cm^{-1}, it is usually several hundreds of cm^{-1} broad and not detected.[27] The bending mode, however, occurs in the region between 1000 and 1500 cm^{-1} (1244 cm^{-1} for PyH^+Cl^-) and is diagnostic. In addition, a combination mode at 1540 cm^{-1} is distinctive for the pyridinium ion.[28] The IR spectrum of $(H_2O)_{0.7}[(py)_{0.129-x}(pyH^+)_x]YbOCl$ (Figure 6) clearly show peaks at 1262 and 1535 cm^{-1}, consistent with the presence of pyH^+.

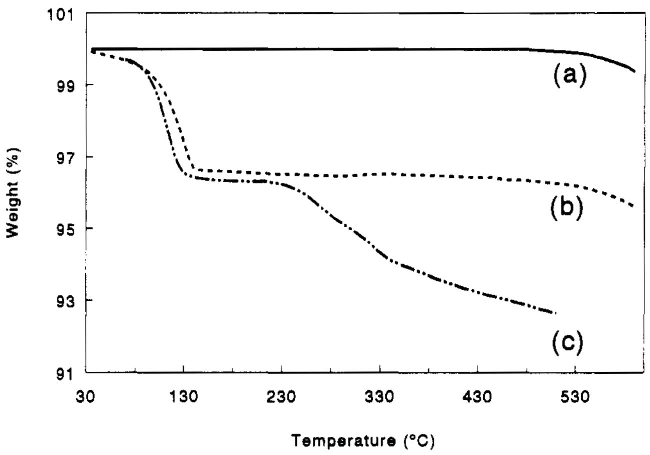

Figure 7. Thermogravimetric analysis curve of (a) YbOCl, (b) $(py)_{0.10}YbOCl$, and (c) $(H_2O)_{0.7}[(py)_{0.129-x}(pyH^+)_x]YbOCl$.

TGA. TGA experiments from room temperature to 600 °C are shown in Figure 7. Dried YbOCl shows no weight loss up to ~530 °C at which temperature decomposition to Yb_2O_3 occurs, as determined by X-ray powder diffraction. Figure 7 also shows the TGA curves for $(py)_{0.10}YbOCl$ and $(H_2O)_{0.7}[(py)_{0.129-x}(pyH^+)_x]YbOCl$. In the case of $(py)_{0.10}YbOCl$, only one weight loss is observed, consistent with one form of pyridine. The rather low temperature of the deintercalation indicates that this species is rather weakly bonded within the layers as is expected for the neutral pyridine molecule. Powder patterns of $(py)_{0.10}YbOCl$ show complete deintercalation at 150 °C. The TGA curve for $(H_2O)_{0.7}[(py)_{0.129-x}(pyH^+)_x]YbOCl$, however, shows two distinctive weight losses and the TGA curve never flattens out. At 107 °C, the first species (the more weakly bonded) is deintercalated and is presumably the pyridine molecule (along with loss of some H_2O). The second weight loss has an onset at ~190 °C and corresponds to the deintercalation of pyridinium ions and loss of H_2O. Figure 1 shows that H_2O is not completely removed from YbOCl until 350 °C. MS analysis of the gases from both weight losses confirm the presence of pyridine. The presence of H_2O cannot be confirmed due to the background of H_2O in the spectrometer. Powder patterns of $(H_2O)_{0.7}[(py)_{0.129-x}(pyH^+)_x]YbOCl$ after treatment at 150 °C (Figure 4) show a small amount of intercalate still present. Treatment at 300 °C results in complete deintercalation of the pyridine and pyridinium as shown in Figure 4. The broad diffraction peaks after the TGA experiment indicate that removal of the pyridinium ions may also partially decompose the host. X-ray powder diffraction of the sample after heating to 510 °C shows significant decomposition to Yb_2O_3.

Reaction Mechanism. Unlike the sodium intercalates, the pyridine intercalation products do not have the characteristic optical spectra associated with Yb^{2+},[11,29] indicating that there is no reduction of the YbOCl host lattice. There is, however, a slight reduction of the *a* lattice parameter upon intercalation. This has also been observed in the high-temperature synthesis of the alkali-metal intercalates of $YOCl$[30] and MXH_x (M = Sc, Y, Gd; X = Cl, Br).[31] This reduction of the lattice parameter may in-

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[28] Parry, E. P. *J. Catal.* **1963**, *2*, 371–379.

[29] Ellis, A. B.; Thomas, A. C.; Schlensener, C. J. *Inorg. Chim. Acta* **1984**, *94*, 20.

[30] Ford, J. E.; Corbett, J. D. *Inorg. Chem.* **1985**, *24*, 4120.

[31] Meyer, G.; Hwu, S.-J.; Wijeyesekera, S.; Corbett, J. D. *Inorg. Chem.* **1986**, *25*, 4811.

dicate an increase in metal–metal bonding that is due to a small amount of electron transfer from the guest to the host. This raised a question concerning the driving force of this intercalation reaction. For most layered materials, intercalation can be described as either a reduction–oxidation or acid–base reaction. For pyridine intercalation into TaS_2, the following redox mechanism has been proposed:[32]

$$2(C_5H_5N) \rightarrow C_{10}H_8N_2 + 2H^+ + 2e^-$$

$$H^+ + C_5H_5N \rightarrow C_5H_5NH^+$$

$$TaS_2 + ne^- + nC_5H_5NH^+ \rightarrow [TaS_2^{n-}(C_5H_5NH^+)_n(C_5H_5N)_y]$$

The presence of molecular cations as well as the proposed orientation of the pyridine[33] within the van der Waals gap provides evidence to support this mechanism for the transition-metal dichalcogenides. Intercalation reactions of pyridine into the transition-metal oxychlorides have been postulated to proceed by the same mechanism.[34] Mössbauer spectroscopy[35] indicates that charge transfer of approximately 0.10 electron/iron atom from pyridine to FeOCl accompanies this reaction. Although the presence of pyridinium ions, and 4,4′-bipyridine in $(py)_x$FeOCl ($x = {}^1/_4, {}^1/_3$) has been inferred from infrared spectroscopy,[34] the production of these species as a result of a redox mechanism is suspect since carefully dried pyridine was not used and a band at 1630 cm^{-1} was incorrectly assigned to the FeOCl matrix. Both pyridine and FeOCl are known to absorb water, and all vibrational modes of FeOCl occur below 700 cm^{-1}.[36] The small amount of charge transfer observed in $(py)_x$FeOCl, combined with the proposed orientation of pyridine (the 2-fold axis of pyridine is perpendicular to the layers) is more consistent with an acid–base description of the intercalation reaction. Pyridine is acting as a Lewis base, forming an adduct through the lone-pair electrons on the nitrogen to the host layers, donating a relatively small amount of charge to FeOCl.

The mechanism for intercalation of pyridine into YbOCl is also more consistent with an acid–base mechanism based on the orientation of the pyridine molecule (determined by X-ray powder diffraction), and the absence of pyH^+ in carefully dried samples. The pyridine molecule is acting as a Lewis base adduct and is coordinated to Yb metal (the only Lewis acid site available), capping the face formed by the three Cl atoms. pyH^+ is not found in the samples prepared with dried, distilled pyridine, and the IR is consistent with pyridine acting as an donor molecule to the YbOCl layers.

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Registry No. $(H_2O)_{0.7}(Py)_{0.129}$YbOCl, 141903-62-0; $(Py)_{0.10}$YbOCl, 141903-63-1; YbOCl, 13759-96-1; $(4\text{-EtPy})_x$YbOCl, 141903-64-2.

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[32] (a) Schöllhorn, R.; Zagefka, H. D.; Butz, T.; Lerf, A. *Mater. Res. Bull.* 1979, *14*, 369. (b) Schöllhorn, R. *Angew. Chem., Int. Ed. Engl.* 1980, *19*, 983.

[33] McDaniel, P. L.; Barbara, T. M.; Jones, J. *J. Phys. Chem.* 1988, *92*, 626.

[34] Salmon, A.; Eckert, H.; Herber, R. H. *J. Chem. Phys.* 1984, *81*, 5206.

[35] Herber, R. H.; Eckert, H. *Phys. Rev. B* 1985, *31*, 34.

[36] (a) Kauzlarich, S. M.; Ellena, J. F.; Stupik, P. D.; Reiff, W. M.; Averill, B. A. *J. Am. Chem. Soc.* 1987, *109*, 4561. (b) Averill, B. A.; Kauzlarich, S. M.; Teo, B. K.; Faber, J., Jr. *Mol. Cryst. Liq. Cryst.* 1985, *120*, 259.