Mesostructured Lamellar Phases Containing Six-Membered Vanadium Borophosphate Cluster Anions

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A series of compounds with the general formula $(NH_4)_x(C_nH_{2n+1}NH_3)_y[(NH_4)\supset V_2P_2BO_{12}]_6 \cdot zH_2O$ ($7 \le n \le 18$, $x + y = 17$) was prepared by reaction of *n*-alkylamines with ammonium vanadium borophosphate, $(NH_4)_{17}[(NH_4)\supset V_2P_2BO_{12}]_6 \cdot 14H_2O$ (NH_4-VBPO). The alkylammonium vanadium borophosphates (alkylammonium-VBPOs) were characterized by powder X-ray diffraction, IR spectroscopy, TEM analysis, thermogravimetric measurements, and elemental analysis. The results show that the structures of the alkylammonium-VBPO phases are composed of H-bonded layers of vanadium borophosphate cluster anions. Within the layers, NH_4 cations and H_2O molecules are H-bonded either to the oxygen atoms of the cluster anions or to each other. The alkylammonium cations occupy the interlayer space and form either a bilayer with a chain orientation of ~47° ($7 \le n \le 12$) or an interdigitated arrangement with a chain orientation of ~90° ($13 \le n \le 18$).

Introduction

Many layered oxides such as silicates, transition metal oxides, hydroxides, phosphates, and arsenates readily intercalate long-chain alkylamines. Some layered alkali transition metal oxides exchange alkali metal cations for alkylammonium ions directly.[1] Recently, interest in these inorganic−organic (surfactant) phases has dramatically increased in part because of the successful synthesis by Mobil of a family of silica-based mesoporous materials called M41S.[2,3] Similar phases formed from cluster anions and surfactants have been relatively less well studied, although several are known. Some recent examples related to the present work are summarized below.

In the structure of dodecylammonium thiostannate, $[Sn_2S_6]^{4-}$ cluster anions form an infinite layer stabilized by H-bonds between neighboring ammonium cations and water molecules.[4] The alkyltrimethylammonium germanium sulfides contain similar layers of unconnected $[Ge_4S_{10}]^{4-}$ cluster anions, separated by an interdigitated arrangement of alkyltrimethylammonium cations.[5,6] Interestingly, these compounds show absorption properties for linear alcohols of various chain lengths.

The cluster anion−surfactant phases have also been used as precursors for the assembly of mesoporous materials. The reaction of cetyltrimethylammonium germanium sulfide, $CTA_4Ge_4S_{10}$, with metal salts in nonaqueous solution results in the formation of hexagonal metal germanium sulfide mesoporous structures in which the metal ions (Co, Ni, Cu, Zn) are coordinated to sulfur atoms in the $[Ge_4S_{10}]$ cluster anions.[7−9] In an alternate synthetic route, the hydrothermal reaction of $Na_4Ge_4S_{10}$, $MnCl_2$, and mesityltrimethylammonium bromide leads to the formation of a mesostructured manganese germanium sulfide with a hexagonal structure.[10] Cetyltrimethylammonium glycometalates form lamellar mesophases that, on hydrolysis, produce well-ordered mesoporous metal oxides.[7,11,12] Interdigitated arrangements of alkyl chains are found between H-bonded layers of dihydrogen phosphate anions in decylammonium dihydrogen phosphate.[7,13,14] Similar alkylammonium phosphate salts containing cyclopentylammonium and octylammonium cations between H-bonded layers of mono-dihydrogen phosphate anions have been reported.[13]

The water-soluble vanadium borophosphate compound $(NH_4)_{17}[(NH_4)\supset V_2P_2BO_{12}]_6 \cdot 14H_2O$ (NH_4-VBPO), containing the cluster anion $[(NH_4)\supset V_2P_2BO_{12}]_6^{17-}$, was first reported by us.[14] In this paper, we describe the results of the assembly of this anion with *n*-alkylammonium cations to form a series of lamellar compounds. Powder X-ray diffraction, infrared spectroscopy, TEM analysis, thermogravimetric measurements and elemental analysis were used to characterize compounds with

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Table 1. Optimized Synthetic Conditions for Alkylammonium-VBPO[a]

C_n	alkylamine − solvent	temperature
C_7	$C_7H_{17}N$ − hexane	RT[b]
C_8	$C_8H_{19}N$ − hexane	RT
C_9	$C_9H_{21}N$ − hexane	RT
C_{10}	$C_{10}H_{23}N$ − hexane	60 °C
C_{11}	$C_{11}H_{25}N$ − hexane	60 °C
C_{12}	$C_{12}H_{27}N{\cdot}HCl$ − hexane	RT
C_{13}	$C_{13}H_{29}N$ − acetone	RT
C_{14}	$C_{14}H_{31}N$ + HCl − hexane	RT
C_{15}	$C_{15}H_{33}N$ − hexane	RT
C_{16}	$C_{16}H_{35}N$ − hexane	RT
C_{17}	$C_{17}H_{37}N$ − hexane	RT
C_{18}	$C_{18}H_{39}N$ − hexane	RT

[a] All reactions used 0.2779 g (0.1 mmol) of NH_4-VBPO. [b] RT = room temperature.

the general compositions $(NH_4)_x(C_nH_{2n+1}NH_3)_y[(NH_4)\supset V_2P_2BO_{12}]_6{\cdot}zH_2O$ ($x + y = 17$, $7 \leq n \leq 18$).

Experimental Section

Synthesis. The compounds were synthesized by two-step reactions. In the first step, $(NH_4)_{18}[V_2P_2BO_{12}]_6{\cdot}14H_2O$ (NH_4-VBPO) was prepared hydrothermally as previously reported.[14] V_2O_3 (0.2248 g, 1.5 mmol), H_3BO_3 (0.3090 g, 5 mmol), H_3PO_4 (0.342 mL, 85 wt % solution in H_2O, 5 mmol), NH_4OH (2 mL, 29.6% solution in H_2O, 15.4 mmol), and H_2O (2 mL) were allowed to react at 160 °C. The resulting blue crystals of NH_4-VBPO were used in the second step of the synthesis. The second reaction step is exemplified for heptylamine. The optimum reaction conditions to obtain single-phase products are summarized in Table 1.

As a typical example, the compound $(NH_4)(heptylamineH)_{17}[V_2P_2BO_{12}]_6{\cdot}12H_2O$ was synthesized by the following procedure. Heptylamine (0.1 mL, 0.67 mmol) in hexane (10 mL) was slowly added to a solution of $(NH_4)_{18}[V_2P_2BO_{12}]_6{\cdot}14H_2O$ (0.277 g, 0.1 mmol) in H_2O (20 mL). The mixture was stirred for 2 h at room temperature. The blue aggregated powder product was filtered, washed with distilled water, and dried at room temperature. Similar reaction conditions were used for the other compounds.

Characterization. The compositions of the products were determined by a combination of thermogravimetric (SDT 2960 DTA-TGA, TA Instruments) and elemental analysis (Galbraith Laboratories, Knoxville, TN). TGA measurements were made in air at a scan rate of 2 °C/min to 800 °C. Interlayer spacings were determined from X-ray diffraction data recorded on a Scintag XDS 2000 automated diffractometer in $\theta-\theta$ geometry with Cu Kα radiation ($\lambda = 1.5406$ Å). The infrared spectra (KBr pellet method) were recorded on a Galaxy FTIR 5000 series spectrometer. The transmission electron microscope (TEM) employed in this work was a JEOL 2000 FX instrument.

Results

Synthesis and Powder-XRD Analysis. The reaction of NH_4-VBPO with *n*-alkylamines leads to the formation of alkylammonium-VBPO phases. Selected powder X-ray diffraction patterns of C_{16}- and C_{18}-VBPO are shown in Figure 1. The first three strong (00*l*) peaks ($l = 1, 2, 3$) at low angles are indicative of the lamellar mesostructures of the compounds. In Figure 1, the intensities are plotted on a logarithmic scale to emphasize the weak reflections. The observed interlayer spacings are determined by the packing of the hydrocarbon chains of the alkylammonium cations in the interlayer space. The interlayer spacings of each product are presented in Table 2. For the compounds with $10 \leq n \leq 14$, two interlayer spacings are shown for reasons discussed below. The observed interlayer spacings for all compounds can be divided into two distinct regions showing the differences in the relative importance of chain packing and van der Waals' interactions between chains (Figure 2).

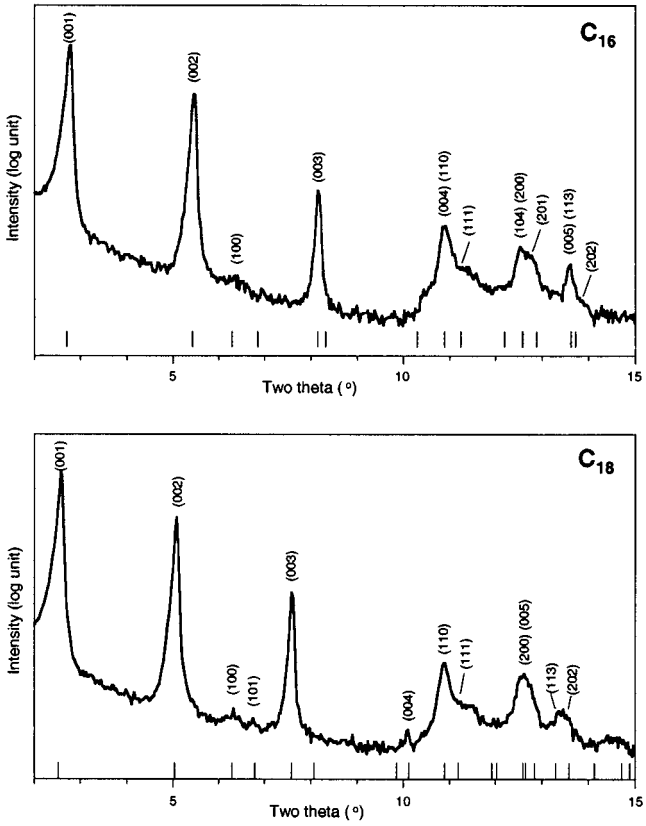

Figure 1. X-ray powder diffraction patterns of C_{16}- and C_{18}-VBPO. The intensity data are given on a logarithmic scale.

Table 2. Interlayer Spacings and CH_2 Asymmetric Stretching Vibrations for Alkylammonium-VBPO

n	interlayer spacing (Å)[a]	CH_2 vibration (cm^{-1})
7	24.15	2928
8	26.10	2926
9	27.55	2924
10[b]	29.86	2922
	28.17	
11[b]	31.61	2922
	28.36	
12[b]	33.38	2920.5
	27.51	
13[b]	28.64	2920.5
	35.14	
14[b]	29.99	2920.5
	38.50	
15	31.04	2920.5
16	32.53	2918.5
17	34.16	2918.5
18	34.97	2918.5

[a] Interlayer spacings are obtained from (003) reflections. [b] Two-phase mixtures are prepared in hexane at room temperature and differently treated to obtain single phases (see Table 1).

The compounds from C_8 to C_9 and from C_{15} to C_{18} were obtained as single phases in hexane at room temperature. For the $C_{10}-C_{14}$ compounds, two-phase mixtures were obtained by using the same reaction conditions. For C_{10} and C_{11}, one phase has an interlayer spacing that lies on the extrapolation of line i in Figure 2, but the other phase has a smaller spacing (see Table 2 and

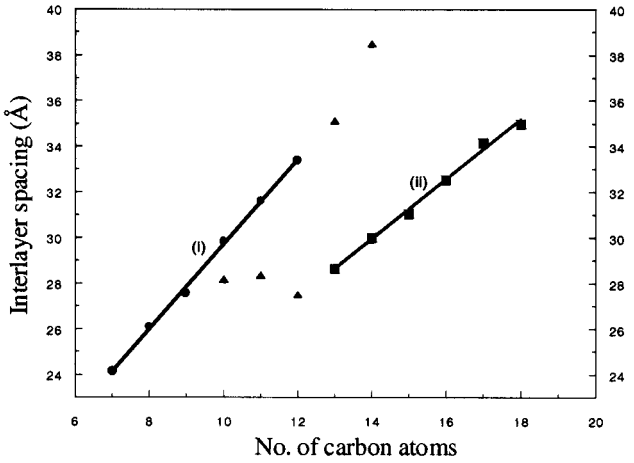

Figure 2. Interlayer spacing vs number of carbon atoms in alkyl chain for the $(NH_4)_x(C_nH_{2n+1}NH_3)_y[(NH_4)\supset V_2P_2BO_{12}]_6 \cdot zH_2O$ phases. The filled triangles indicate the interlayer spacing of the minor phase observed in $C_{10}-C_{14}$ reactions.

Figure 2). Pure phases of the C_{10} and C_{11} compounds (upper line) were prepared by heating the reactants at 60 °C for 2 h. For C_{12} and C_{13}, the two interlayer spacings lie on lines i and ii. For C_{12}, a pure phase with the higher interlayer spacing (line i) was obtained by using $C_{12}H_{27}N \cdot HCl$ as one of the reactants. A single-phase product with an interlayer spacing that lies on the extrapolation of line ii could not be obtained by varying the reaction conditions. The C_{13} phase with the larger spacing was not observed when the solvent was changed to acetone. However, a single phase containing only the shorter spacing on line ii cannot be synthesized, even though a larger amount of the phase can be obtained by heating the solution. For the C_{14} compound, one of the phases has a longer spacing than expected from the extrapolation of line i. A single phase of the C_{14} compound with the line ii spacing was obtained by adding a drop of concentrated HCl.

Compositional Study (TGA and Elemental Analysis). Thermogravimetric analysis results show that the evolution of crystal water, NH_3, carbon oxides, and H_2O molecules from the structure and the oxidation of V^{4+} to V^{5+} are completed between ~600 and ~700 °C in several steps. For the longer alkylammonium chains, the evolution of water occurs below 100 °C. The weight remains constant until ~200 °C, where decomposition begins. A typical TGA curve of C_{18}-VBPO is shown in Figure 3. The compounds with shorter alkylammonium chains ($n < 12$) decompose over a wider temperature range without distinct steps. The compositions of each compound as determined by elemental analysis and TGA measurements are shown in Table 3.

IR Spectroscopy. Selected IR spectra are shown in Figure 4. The characteristic infrared spectra in the region of 1200−400 cm^{-1}, corresponding to V═O, P−O, and B−O vibrations, confirm the presence of $[(NH_4)\supset(VO)_2P_2BO_{10}]_6$ cluster anions. The positions of the CH_2 asymmetric stretching vibrations in the IR spectra provide information on the extent to which the alkyl chains of the alkylammonium cations have crystalline or liquidlike structures. The IR spectra of a well-ordered trans configuration and a disordered gauche defect structure show bands at ~2918 cm^{-1} and above 2925 cm^{-1}, respectively. In the alkylammonium-VPBO compounds, as the alkyl chain length increases, the wavenumber of the CH_2 asymmetric stretching vibration gradually decreases to 2918.5 cm^{-1}, indicating that, as n increases, the chains become more ordered and closer packed.

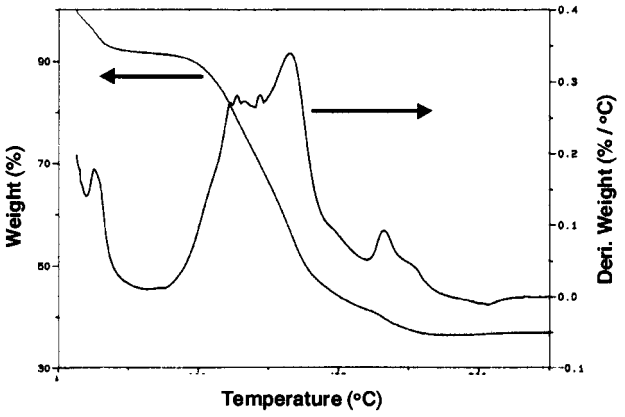

Figure 3. Thermogravimetric analysis data for C_{18}-VBPO.

Table 3. Compositions of the Alkylammonium-VPBO Compounds Based on Elemental Analysis and TGA[a]

	V	*y*	*N*	*y* (*z*) (based on TGA)[b]
C_7	12	15.9	17.0	≤17
C_8	12	15.7	18.8	≤16
C_9	12	14.4	18.6	≤14
C_{10}	12	16.2	18.6	≤15
C_{11}	12	16.6	19.2	≤16
C_{12}	12	15.5	18.2	16 ($z = 31$)
C_{13}	12	12.5	19.9	14 ($z = 21$)
C_{14}	12	13.2	18.9	12 ($z = 21$)
C_{15}	12	12.3	18.9	12 ($z = 18$)
C_{16}	12	13.7	19.9	13 ($z = 26$)
C_{17}	12	13.5	19.0	12 ($z = 19$)
C_{18}	12	13.3	19.2	12 ($z = 21$)

[a] The left three columns show the calculated mole ratios relative to 12 vanadium atoms in $(NH_4)_x(C_nH_{2n+1}NH_3)_y[(NH_4)\supset V_2P_2BO_{12}]_6 \cdot zH_2O$ ($x + y = 17$, $7 \le n \le 18$). [b] The water contents (z values) for compounds with $n \ge 12$ were obtained assuming that the evolution of water occurs below 100°C.

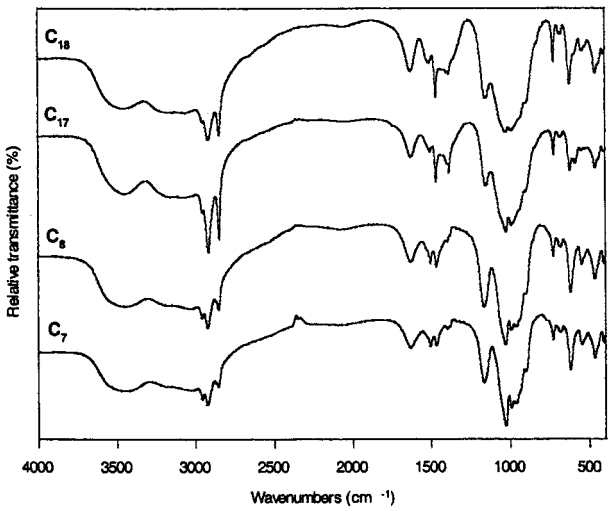

Figure 4. Representative infrared spectra for the alkylammonium-VPBO phases.

Discussion

The interlayer spacing increases as the number of carbon atoms in the alkyl chains is increased (Figure

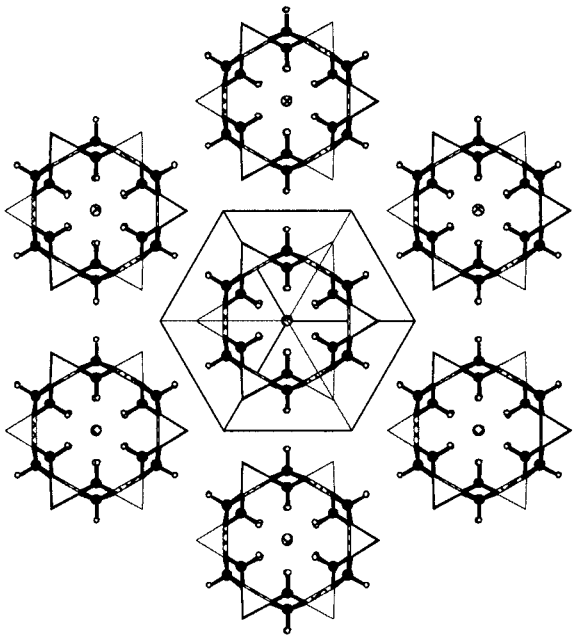

Figure 5. Layers of six-membered vanadium borophosphate cluster anions in NH_4-VPBO. The PO_4 and BO_4 units are shown as filled and crosshatched tetrahedra, respectively, the vanadium and oxygen atoms as filled and open circles, respectively, and the nitrogen atoms as crosshatched circles.

2). In region i, a least-squares fit to the data gives

$$d = 1.856n + 11.141 \text{ Å}$$

where d is the interlayer spacing and n is the number of carbon atoms in the alkylammonium cations. The increment of 1.856 Å per carbon atom implies bilayer arrangements of the alkylammonium cations between the layers. The slope of this line gives the mean angle α that the chains make with the layer surface by the relation $\alpha = \sin^{-1}[1.856/(1.27 \times 2)] = 46.9°$, where 1.27 Å is the length increment per carbon atom in a linear all-trans chain.

In region ii, a least-squares fit to the data gives

$$d = 1.304n + 11.666 \text{ Å}$$

If the molecules in this region have the same bilayer arrangement of alklyammonium cations as do those in region i, then the tilt angle should be $\alpha = 30.9°$, which is indicative of weaker van der Waals' interactions between the alkylammonium cations than in region i. However, in general, as the chain length increases, the van der Waals' interactions also increase, which should result in a more ordered arrangement and a substantial increase of the tilt angle α. Thus, an interdigitated arrangement is more likely in region ii with a perpendicular direction of chains, $\alpha \approx 90°$. This model is supported by the infrared data, which indicate that, for $C_{16}-C_{18}$, the alkyl chains adopt an all-trans configuration (observed CH_2 asymmetric stretching vibration, 2918 cm^{-1} for C_{16}, C_{17}, and C_{18}).

Previously reported VBPOs, such as NH_4VPBO (Figure 5), have layer structures in which NH_4^+ and H_2O are H-bonded either to the oxygen atoms of the cluster anions or to each other.[14−16] In the X-ray data for the alkylammonium-VPBO compounds, several weak reflections indicate a similar hexagonal arrangement (Figure 5). For C_{18}-VBPO, assuming that the next peak after the (00l) (l = 1, 2, 3, 4) peaks corresponds to the (110) reflection, the other observed peak positions are in good agreement with those calculated for the hexagonal cell parameters $a = 16.22(1)$ Å and $c = 34.968(5)$ Å. Between (002) and (003), two additional small peaks corresponding to the (100) and (101) reflections are observed. Also, the lines in the X-ray powder diffraction pattern of C_{16}-VBPO are well indexed when the same value of a = 16.22 Å is used but with a smaller value of $c = 32.526$ Å (Figure 1). In the other alkylammonium-VBPO phases, the same lattice parameter, a = 16.22 Å, is observed independent of the chain lengths of the alkylamines in the structures. The hexagonal lattice parameter (a = 16.22 Å) is in good agreement with the lattice parameter $a = 16.5490(9)$ Å observed in NH_4-VBPO (Figure 5).

Extrapolation of the data to $n = 0$ gives intercepts of 11.141 and 11.666 Å for regions i and ii, respectively. The values are larger than the value of 10.36 Å observed for the interlayer distance between H-bonded $[(NH_4)\supset V_2P_2BO_{12}]_6^{17-}$ layers in NH_4-VBPO.[14] The increase might reflect some buckling of the layers of the alkylammonium-VBPO phases caused by the interactions between the alkyl chains in the alkylammonium cations. The smaller a value is also consistent with some layer distortion.

The effective interlayer areas per alkyl chain based on the structure of NH_4-VBPO are 29.8 and 39.7 $Å^2$, assuming that the compounds in regions i and ii have general compositions of $(NH_4)_2(alkylamineH)_{16}[V_2P_2BO_{12}]_6 \cdot zH_2O$ and $(NH_4)_6(alkylamineH)_{12}[V_2P_2BO_{12}]_6 \cdot zH_2O$, respectively. The linear all-trans hydrocarbon chain in polyethylene has a cross-sectional area of 18.2 $Å^2$. The cross-sectional area of 39.7 $Å^2$ in region ii is almost twice the value of 18.2 $Å^2$ in polyethylene, which strongly supports an interdigitated configuration with a perpendicular orientation of the chains.[17]

The increase in layer spacing observed when the alkylammonium chain length is increased by one carbon is plotted as interlayer spacing vs carbon number (Figure 2). Jacobson et al. showed that a regular odd−even alteration in interlayer spacing is a consequence of a perpendicular orientation of the C−N bond and a chain angle of ∼68° with respect to the layers.[18] However, in this case no odd−even alteration is apparent in either region i or region ii, consistent with the disorder in region i and the 90° chain orientation in region ii.

The electron microscopy results are consistent with the data obtained from X-ray diffraction. A TEM image of the C_{15}-VBPO compound is shown in Figure 6. The figure shows a layered structure with a layer separation of ca. 32 Å, in agreement with the d spacing calculated from the X-ray diffraction data. Also, the thickness of the layer is approximately 10 Å, in excellent agreement with the calculated thickness of $[(NH_4)\supset V_2P_2BO_{12}]_6$

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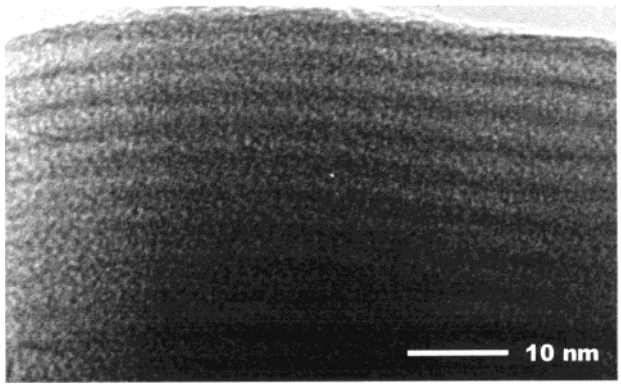

Figure 6. Transmission electron micrograph of C_{15}-VBPO.

cluster anions. The TEM results confirm the lamellar structure of the alkylammonium-VBPO phases.

In summary, a series of compounds with the general formula $(NH_4)_x(C_nH_{2n+1}NH_3)_y[(NH_4)\supset V_2P_2BO_{12}]_6 \cdot zH_2O$ ($7 \leq n \leq 18$) was prepared by ion-exchange reactions of *n*-alkylamines with NH_4-VBPO. Ammonium cations between the cluster anions are either fully or partially exchanged by *n*-alkylammonium cations immediately upon reaction. The XRD data reveal that the structures of alkylammonium-VBPO phases consist of H-bonded layers of vanadium borophosphate cluster anions in a hexagonal arrangement, between which the alkylammonium cations either lie in a bilayer with a chain orientation of ~47° ($7 \leq n \leq 12$) or are interdigitated with a chain orientation of ~90° ($13 \leq n \leq 18$). The different packings of the alkylammonium cations are determined by the interactions between the alkyl chains, and the transition between two different packing arrangements occurs between C_{12}- and C_{13}-VBPO.

The alkylammonium-VBPO phases become less soluble with increasing *n*. Thus, NH_4-VBPO is water-soluble, whereas C_7-VBPO is not soluble in water but dissolves in either THF/water or acetone/water. Thus far, we have not been successful in growing single crystals from solution suitable for X-ray diffraction.

In conclusion, we have demonstrated that well-ordered lamellar mesophases can be obtained from large inorganic cluster anions and alkylammonium cations. We are at present investigating the use of other surfactants and coupling agents to form similar mesostructures with permanent porosity.

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Supporting Information Available: Tables of elemental analysis results, observed IR vibration modes, and X-ray powder patterns for all the compounds (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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