Microporous Montmorillonites Expanded with Alumina Clusters and $M[(\mu\text{-}OH)Cu(\mu\text{-}OCH_2CH_2NEt_2)]_6(ClO_4)_3$, (M = Al, Ga, and Fe), or $Cr[(\mu\text{-}OCH_3)(\mu\text{-}OCH_2CH_2NEt_2)CuCl]_3$ Complexes

S. M. Thomas,[†,‡] J. A. Bertrand,[‡] M. L. Occelli,*[,†] F. Huggins,[§] and S. A. C. Gould[||]

Zeolites and Clays Program, GTRI, Georgia Institute of Technology, Atlanta, Georgia 30332-0827,
Department of Chemistry and Biochemistry, Georgia Institute of Technology,
Atlanta, Georgia 30332-0400, University of Kentucky, Lexington, Kentucky 40506-0043, and
W. M. Keck Science Center, Claremont Colleges, Claremont, California 91711

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Expanded clays bipillared with $[Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{7+}$ ions and with hexameric Cu complexes such as $M[(\mu\text{-}OH)Cu(\mu\text{-}OCH_2CH_2NEt_2)]_6(ClO_4)_3$, or with $M[(\mu\text{-}OH)Cu(\mu\text{-}OCH_2CH_2NEt_2)]_6(PF_6)_3$ where M = Fe, Al, Ga, form microporous materials whose stability and microporosity depend mainly on the identity of the hexamer central metal atom. In fact, a general decrease in thermal stability, interlamellar heights, surface areas, and pore volumes was noted when, in the (Cu,M) hexamer, M changed from gallium to aluminum to iron. Mossbauer results have indicated that only Fe^{3+} in octahedral coordination is present in the iron-containing bi-PILC samples (bi-PILC = bipillared interlayered clays). It is believed that metals such as Fe^{3+} and Cu^{2+} can interact with the interlamellar Keggin ions thereby decreasing the stability of the alumina pillars. In contrast, the intermediate Al_{13}-PILC structure is least affected when the more stable Cr complex is used. Bi-PILC materials containing 2.7−3.4% Cr stable to 500 °C have been obtained. The low polarity of the chosen solvent (acetonitrile) appears to inhibit the back-exchange of the intermediate PILC's Keggin ions with the hexameric Cu complexes. Elemental analysis together with XRD results suggests that the primary intercalation pathway was diffusion or ion exchange when $Cr[(\mu\text{-}OCH_3)(\mu\text{-}OCH_2CH_2NEt_2)CuCl]_3$ or $M[(\mu\text{-}OH)Cu(\mu\text{-}OCH_2CH_2NEt_2)]_6(ClO_4)_3$, respectively, was used. In all preparations, bi-PILC were produced containing complexes that suffered ligand losses during the synthesis reaction. Molecular scale AFM images have shown that these complexes can be found also outside the clay interlamellar space.

Introduction

The use of clays such as montmorillonites to catalyze organic synthesis offers advantages over traditional homogeneous catalysts that include easy catalyst recovery and, possibly, shape selectivity effects resulting from the catalyst's unique architecture. Problems associated with the handling of moisture sensitive homogeneous catalysts such as $TiCl_4$ and Ph_3CCl_4 are also avoided.[1] Catalytic activity and selectivity can be influenced by the choice of the cations used to charge compensate the negative layer charge on the clay silicate layers.[1]

In a companion paper[2] it was shown that the thermal stability of montmorillonites expanded with a Co trimer can be dramatically increased by introducing a second pillar such as $[Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{7+}$ ions. After calcination in air at 500 °C, alumina clusters are formed that impart to the cobalt-containing expanded clay its stability. Best results were obtained by first ion-exchanging the clay charge compensating cations with $[Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{7+}$ ions followed by a second ion exchange step to replace some of the Al species in the interlamellar space with Co complexes. Microporous Co-containing materials with *d* spacing in the 1.40−1.75 nm range at 500 °C were thus obtained.[2]

The purpose of this paper is to report the synthesis of bipillared interlayered clays (bi-PILC) in which the hexameric series $M[(\mu\text{-}OH)Cu(\mu OCH_2CH_2NEt_2)]_6(ClO_4)_3$ (where M = Al, Fe, Ga) or the neutral molecule $Cr[(\mu\text{-}OCH_3)(\mu\text{-}OCH_2CH_2NEt_2)CuCl]_3$ have been introduced into a clay previously expanded with $[Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{7+}$ ions. The objective of the work is to produce expanded structures containing metal complexes that will not interact with the clay silicate layer so that on calcination catalytically active metal oxide centers will be formed.

Experimental Section

Preparation of Pillaring Agents. The procedure for the preparation of metal complexes such as $M[(\mu\text{-}OH)Cu(\mu\text{-}OCH_2CH_2NEt_2)]_6(ClO_4)_3$ (M = Fe, Al, Ga) was adapted from that developed by Beckler et al.[3] Copper(II) perchlorate hexahydrate (14.8 g, 40 mmol, Aldrich) was dissolved in methanol (50 mL) and heated, with stirring, until boiling. *N,N*-Diethyl-2-aminoethanol (9.38 g, 80 mmol, Aldrich) was mixed with methanol (25 mL) and added to the stirred copper solution. The solution turned a milky blue-green coloration. Reagent-grade potassium hydroxide (5.13 g, 90 mmol) was dissolved in methanol (30 mL) and slowly added to the copper solution. This mixture was boiled for 15 min and then filtered. The purple filtrate was heated to a boil, and

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* Corresponding author.

[†] Zeolites and Clays Program, GTRI, Georgia Institute of Technology.

[‡] Department of Chemistry and Biochemistry, Georgia Institute of Technology.

[§] University of Kentucky.

[||] Claremont Colleges.

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$Al(NO_3)_3{\cdot}6H_2O$ (2.62 g, 7 mmol, Fisher) or $MCl_3{\cdot}6H_2O$ (M = Fe, 2.63 g, 7 mmol, or Ga, 1.23 g, 7 mmol, Fisher) dissolved in methanol (25 mL) was added. The resulting solution was held at 60 °C for 15 min and then crystallized in an ice bath for 2 h. The precipitate was twice recrystallized from acetonitrile. The green, iron-containing compound (43% yield) and azure aluminum- and gallium-containing crystals (69% and 54% yields, respectively) were all positively identified using elemental analysis and powder X-ray diffraction.

The procedure for the preparation of $M[(\mu\text{-}OH)Cu(\mu\text{-}OCH_2CH_2NEt_2)]_6(PF_6)_3$ was adapted from the one developed by Liu et al.[4] This salt was used to study the thermal stability of the $M[(\mu\text{-}OH)Cu(\mu\text{-}OCH_2CH_2NEt_2)]^{3+}$ cation. The preparation of $Cr[(\mu\text{-}OCH_3)(\mu\text{-}OCH_2CH_2NEt_2)CuCl]_3$ crystals was similar to the one used to prepare hexameric species[3] described above.

Preparation of Bipillared Interlayered Clays (Bi-PILC). All PILC were prepared using a sample of Na-bentonite, (bentolite-H) obtained from Southern Clay Products, Inc., Gonzales, TX.[10] Bi-PILC containing $M[(\mu\text{-}OH)Cu(\mu\text{-}OCH_2CH_2NEt_2)]_6^{3+}$ cations were prepared by first replacing the clay charge compensating Na and Ca ions with $[Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{7+}$ ions using a procedure described in detail elsewhere.[10] The Al-PILC intermediate thus obtained was then suspended in acetonitrile (2 L, Fisher) and stirred at 80 °C for 6 h. The suspension was centrifuged and reslurried repeatedly in acetonitrile (6 L, total). Exhaustive removal of all water was necessitated by the instability of the copper complexes in aqueous solution. The Al-PILC was then suspended in acetonitrile (2 L), and varying amounts (0.2−0.8 mequiv/g of clay) of $M[(\mu\text{-}OH)Cu(\mu\text{-}OCH_2CH_2NEt_2)]_6(ClO_4)_3$ (M = Al, Fe, or Ga) were introduced by Soxhlet into the slurry. The samples were pillared using Soxhlet extraction for 24−72 h, depending upon the amount of complex used. The pillared products were stirred at room temperature for another 8 h and then were filtered. All samples were washed with hot acetonitrile until a colorless filtrate was observed. The resultant materials were air-dried for 48 h and then oven-dried for another 24 h at 100 °C under vacuum.

Similarly, Cr-containing bi-PILC materials were prepared by reacting Al-PILC with $Cr[(\mu\text{-}OCH_3)Cu(\mu\text{-}OCH_2CH_2NEt_2)Cl]_3$ solutions. That is, the Al-PILC was suspended in acetonitrile (1 L), and varying amounts (0.4−0.8 mequiv/g of clay) of $Cr[(\mu\text{-}OCH_3)Cu(\mu\text{-}OCH_2CH_2NEt_2)Cl]_3$ were introduced by Soxhlet into the slurry. The samples were refluxed for 24−72 h, depending upon the amount of complex used. The pillared products were stirred at room temperature for another 8 h and then filtered. All of the samples were washed with hot acetonitrile until a colorless filtrate was observed (initially filtrates were dark green). The resultant materials were first air-dried for 48 h, and then oven-dried for 24 h at 100 °C under vacuum.

Elemental Analysis. Elemental analysis was performed by Applied Technical Services, Inc., in Marietta, GA, and by Galbraith Laboratories in Knoxville, TN, using atomic absorption and (ICP) atomic emission techniques. Trace metal amounts (<0.01%) were not reported. Carbon, nitrogen, and halide analyses were performed by Atlantic Microlab, Inc., in Norcross, GA. Carbon and nitrogen analyses were obtained using combustion methods and reported to have an uncertainty of ±0.3 wt %. Quantitative analysis for ClO_4^- was accomplished using the procedure of Geilmann and Voight[5] as modified by Beckler.[4]

Powder X-ray Diffraction. Powder X-ray data was collected on a Scintag X1 diffractometer with unfiltered Cu Kα radiation, fixed divergence slits, and a Scintag Peltier cooled solid state detector. A convergent slit width of 1 mm and a scatter slit width of 2 mm were employed for the beam source; a receiving slit width of 0.3 and scatter slit width of 0.5 mm were used for the detector. Data was analyzed using version 1.12 DMSNT software. Scans were run in continuous mode at a rate of 2°/min or less.

Thermogravimetric Analysis. All thermogravimetric analyses (TGA and DTA) were obtained on a Seiko 210/310 analyzer equipped with 3.0 version software or a Perkin-Elmer 7.0 analyzer. Samples were heated at a rate of 10.0°/min to 100 °C in flowing (80 mL/min) nitrogen or air. The temperature was held at 100 °C for 30 min to induce the loss of adsorbed water and solvent from the PILC samples. Then the temperature was raised to 600 °C at a rate of 5.0°/min. Data was collected during this heating period.

Surface Analysis. Surface area (SA) and pore volume (PV) were measured by nitrogen sorption at 77 K with an ASAP-2010 porosimeter from Micromeritics. Prior to nitrogen adsorption, the samples were degassed in a vacuum at their calcination temperature for at least 16 h. Pore size distributions were obtained with density functional theory methods assuming slitlike pores.[6,7] The DFT-Plus software package used was from Micromeritics.

Mossbauer Spectroscopy. Mossbauer spectra of the original montmorillonite, the (Cu,Fe) hexamer, and the pillared montmorillonite were obtained at room temperature at one end of a dual-ended Mossbauer driving unit from Halder Elektronik, GMBh, interfaced to a 286 personal computer via Canberra AccuSpec MCS/PHA boards. A calibration spectrum of metallic iron was obtained simultaneously at the opposite end of the drive. The sources on both ends of the driving unit consisted of Co in a palladium matrix. The spectra were acquired in symmetric constant acceleration mode in two groups of 512 channels for at least 72 h owing to the small amounts of iron present in the materials. All spectra were recorded over a limited velocity range of only +4 mm/s as no magnetic phases were anticipated to be present. Spectral analysis consisted of first calibrating the velocity scale of each unknown spectrum according to its corresponding calibration spectrum based on the positions of the four inner peaks of metallic iron at ±0.84 and ±3.08 mm/s. The unknown data were then fitted using a least-squares fitting routine with either two or three quadrupole doublets, each of which was composed of two identical peaks of Lorentzian line shape. As the spectra were relatively weak, there was some ambiguity in exactly how many doublets to include in the fit. The fits reported here are basically the simplest acceptable fits, with χ^2 values less than 600 in each case.

Atomic Force Microscopy (AFM). AFM was performed using a contact mode microscope equipped with a 120 μm Si_3N_4, integral-tipped cantilever. Pillared montmorillonite samples were pressed at 10 000 lb into wafers that were then glued onto steel disks with resin. After the glue dried, the AFM tip was carefully placed onto the wafer; images were acquired within a few seconds. The utility of AFM to characterize clays[8] and the microscope used in this research have been discussed elsewhere.[9]

Results

PILC Synthesis. Expanded clays were prepared using a sample of Na-bentonite (bentolite-H) obtained from Southern Clay Products, Inc., of Gonzales, TX. The pillaring of montmorillonites with aluminum chlorhydroxide (ACH) solutions (Reheis's Chlorhydrol) to generate heat stable Al_{13}-PILC materials has been discussed in detail elsewhere.[10] The back-exchange reactions of Al species from the intermediate Al_{13}-PILC with $M[(\mu\text{-}OH)Cu(\mu\text{-}OCH_2CH_2NEt_2)]_6(ClO_4)_3$ (M = Fe, Al, Ga) solutions generated colored filtrates, indicating that partial decomposition of the hexamers probably occurred during the pillaring reaction. Furthermore, the filtrates' color deepened with increasing the amount of complex added during synthesis, indicating that an exchange maximum had been reached when the reacting mixture contained less than 0.2 mequiv complex/g clay.

Similarly, when the intermediate Al_{13}-PILC was reacted with solutions of $Cr[(\mu\text{-}CH_3)Cu(\mu\text{-}OCH_2CH_2NEt_2)Cl]_3$, filtrates were dark green from the excess complex remaining in solution. The chromium complex is a neutral species, and its occlusion in the Al_{13}-PILC is probably controlled by a diffusion phenomena.

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Table 1. Elemental Analysis for Several Bi-PILC Samples Containing Cu or Cr Complexes as Well as Keggin Ions

sample	% Cu	% Al	% Ga	% Fe	% Si	% Na	% Ca	% Cr
1. AlCu-12	4.7	10.40			23.2	0.068		
2. AlCu-13	3.3	10.39			24.3	0.070		
3. AlCu-14	2.6	10.70			25.4	0.081		
4. AlCu-15	1.6	11.70			25.7	0.068		
5. FeCu-3	3.80	10.33		1.30	25.3	0.072	0.027	
6. FeCu-4	1.44	10.43		0.93	27.3	0.063	0.039	
7. FeCu-5	1.67	10.43		1.14	24.5	0.073	0.031	
8. FeCu-6	3.52	9.30		1.31	23.7	0.062	0.030	
9. GaCu-1	4.47	9.33	1.21		23.7	0.098		
10. GaCu-2	3.47	9.98	0.88		23.9	0.087		
11. GaCu-3	3.23	9.89	0.97		25.1	0.12		
12. GaCu-4	1.40	10.00	0.35		24.9	0.10		
13. CrCu-1	3.39	14.60			28.3	0.41	0.024	0.88
14. CrCu-3	2.78	13.40			29.6	0.41	0.036	0.93
15. Al-PILC		12.10		0.51	27.9	0.083	0.040	
16. bent. H		6.70		0.51	32.2	1.780	1.070	

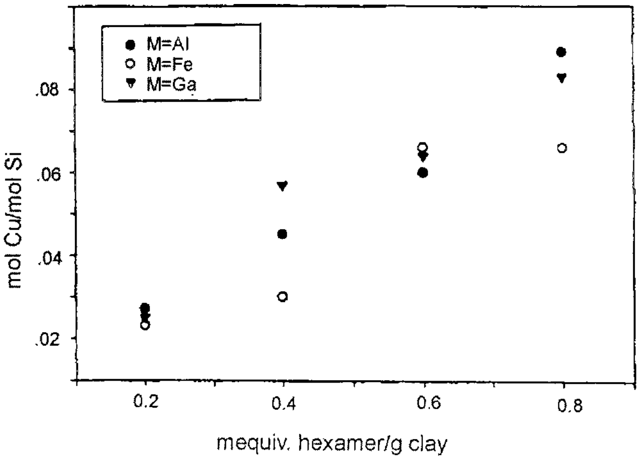

Figure 1. Correlation between bi-PILC Cu incorporation and the bulk solution Cu concentration.

The blue coloration of the washed samples was attributed to the complex partial decomposition during bi-PILC synthesis.

Elemental Analyses. The elemental weight percentages as determined by analysis are given in Table 1.The parent clay contains 2.7 wt % MgO and trace amounts (0.10 wt %) of K_2O. This Mg concentration is unaffected by the pillaring reactions, indicating that Mg (as expected) is located in the clay octahedral layer and therefore unavailable to ion exchange. The charge compensating Na and Ca ions are instead removed during Al_{13}-PILC preparation; see Table 1. The ratio of copper to the central metal should be 6 if the $M[(\mu\text{-OH})Cu(\mu\text{-OCH}_2CH_2NEt_2)]_6(ClO_4)_3$ hexamers remain intact during the ion exchange reaction with the Al_{13}-PILC. However, M/Cu experimental molar ratios are in the 2.0−4.5 range, indicating that partial decomposition of the Cu complexes has occurred during bi-PILC preparation.

Copper loadings in bi-PILC samples increase with increasing Cu concentration in the bulk solution, Figure 1. However, the percent Cu intercalated in the Al_{13}-PILC does not. In fact, samples that have the highest (70−85%) Cu incorporation are those prepared from reaction mixtures with the lowest (0.03−0.07) Cu/Si ratios. It is believed that a concentration dependent equilibrium exists between interlamellar Cu and the Cu complex in solution. Initially, at low hexamer concentrations, accumulation of interlamellar copper is minimal, so the equilibrium favors intercalation. As the loading increases, the back-exchange reaction begins to gain importance and the percent metal incorporation decreases. It should be noted that the average metal percentage incorporated is not identical for the three different hexamers but rather increases in the following order: Fe < Al < Ga. If a simple ion exchange was taking place between the hexamer and the extraframework Al species, the Al_{13}/Si ratio should decrease with increasing Cu/Si values in the bi-PILC samples. However, no such correlation exists, probably because under the synthesis conditions used lower molecular weight Al oligomers as well as Keggin ions are present in the clay interlamellar space. In fact, the total amount of aluminum in bi-PILC samples containing Cu hexamers is generally less than in the reference Al_{13}-PILC; see Table 1. The bi-PILC samples in Table 1 have similar Na and Ca loadings so it is unlikely that residual charge compensating mono- and divalent cations have been replaced by a copper species. In addition, the absence of perchlorates indicates that salt occlusion is negligible. Therefore, in these bi-PILC, ion exchange is believed to be the dominant pathway for Cu incorporation.

The 2.78% Cu in materials prepared with the neutral $Cr[(\mu\text{-OCH}_3)Cu(OCH_2CH_2NEt_2Cl)]_3$ complex demonstrates that Cu incorporation can be achieved without the benefit of ion exchange; see Table 1. In fact, these are the only bi-PILC samples containing a greater concentration of Al (and Na) than the intermediate Al_{13}-PILC; Table 1. In this case, complex occlusion has been attributed to a diffusion phenomenon; as a result, the sample contains 1.1 wt % chloride impurities. Results in Table 1 indicate that the Cr-containing samples have Al_{13}/Si molar ratios in the 0.019−0.025 range adequate for thermal stability to 500 °C.[10]

Powder XRD Results. Powder X-ray diffractograms of montmorillonite pillared with the Keggin ions exhibits a characteristic *d*(001) peak of 1.9−2.0 nm. This spacing contracts to approximately 1.7−1.8 nm at 500 °C when the clay contains at least 0.122 mmol of Keggin ion/g of clay.[10] This pillar density allows the dehydroxylation of the Keggin ions and the rearrangement of its alumina clusters to form stable pillars without affecting the expanded structure stability.[11] In a companion paper,[10] it was shown that an Al_{13}-PILC sample containing 0.0102 mol of Al_{13}/mol of Si collapsed upon calcination at 500 °C while a sample containing 0.0121 mol of Al_{13}/mol of Si did not. The moles of Keggin ion per mole of silicon in bi-PILC samples prepared with aluminum hexamers were determined by assuming a 6/1 ratio between the Cu and the hexamer central metal ion. That is,

$$\text{mol of Al}_{13}\text{/mol of Si} = \{(\text{mol of Al}_{\text{Tot}}\text{/mol of Si}) - (\text{mol of Al}_{\text{Clay}}\text{/mol of Si}) - [(\text{mol of Cu/mol of Si})(1/6)]\}/13$$

Results in Table 1 indicate that these bi-PILC samples possess Al_{13}/Si molar ratios greater than 0.012 and that therefore they should contain sufficient Al_{13} pillars for thermal stability in air to 500 °C.

The powder X-ray diffractogram for the bi-PILC sample containing 2.7% Cu from $Cr[(\mu\text{-OCH}_3)Cu(\mu\text{-OCH}_2CH_2NEt_2Cl)]_3$ exhibits a sharp, intense *d*(001) peak with a spacing of 1.95 nm. As expected from their Al_{13}/Si molar ratios, the layers did not collapse at 500 °C and alumina clusters, from the dehydroxylation of the Keggin ions, appear to be the structure-supporting pillars. In contrast, bi-PILC samples, prepared from $M[(\mu\text{-OH})Cu(\mu\text{-OCH}_2CH_2NEt_2]_6(ClO_4)_3$ (M = Al, Fe, Ga) solutions, generate expanded structures that, although they contain enough Al_{13} ions for thermal stability in air, suffer structural degradation upon heating at $T > 400$ °C; their *d*(001)

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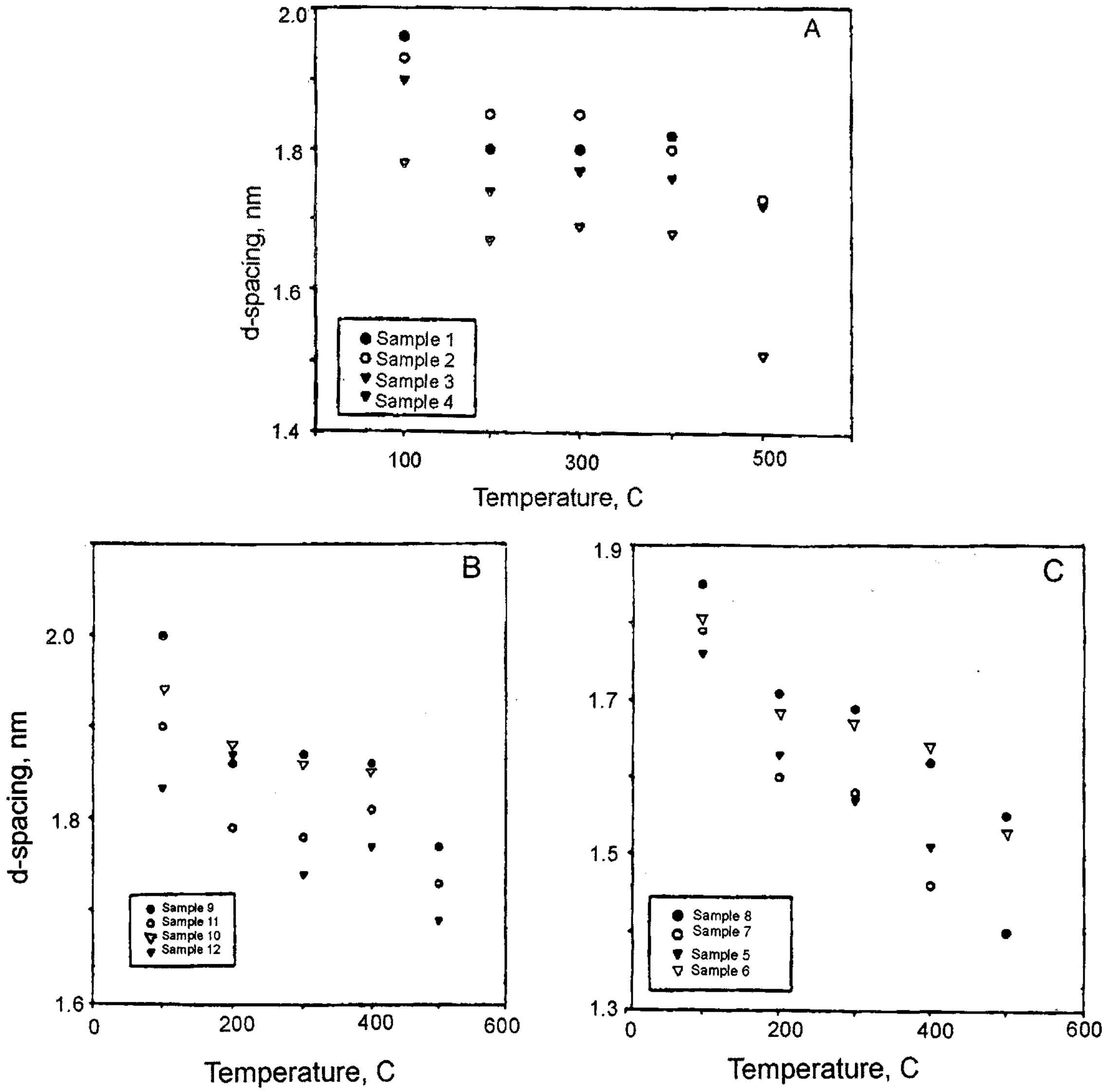

Figure 2. Calcination temperature effects on bi-PILC materials containing M[(μ-OH)Cu(μ-OCH$_2$CH$_2$NEt$_2$)]$_6^{3+}$ ions where (A) M = Al, (B) M = Ga, and (C) M = Fe.

spacings decrease to 1.4−1.6 nm at 500 °C; Figure 2A−C. These XRD results, together with the lack of correlation between the amount of Keggin ions (i.e., extraframework aluminum) in the sample and observed interlayer spacing at 500 °C, suggest that the hexamer complexes, after undergoing partial decomposition, interact with the Keggin ions, thereby decreasing their thermal stability.

In general, after calcination the *d* spacings increase from iron- to aluminum- to gallium-containing samples. Thus the identity of the central metal may affect the interlamellar stability of the three complexes; Figure 2A−C. The bi-PILC stability in the 100−500 °C temperature range increases in the order Fe < Al < Ga. If the Cu complex is decomposing, Cu^{2+} may be chemisorbing to the =AlOH and −AlOH$_2$ groups of the Keggin ion. These interactions have been observed in other Cu-containing, Al-PILC materials.[12−15] However, the effects of these interactions on the pillared clay thermal stability were not reported. Similarly, if the complex were decomposing, the central metal atom would also be free to interact with the Keggin ions. It has been reported that Fe^{3+} ions can replace the Keggin ion central Al(IV) atom and generate pillared clays containing both Al and Fe.[16,17] The pillared clay thermal stability was reduced after the ion exchange step.[17] This observation could explain the low thermal stability of bi-PILC samples containing the (Cu,Fe) hexamer, see Figure 2C.

Thermogravimetric Analyses. TGA data for the intermediate Al$_{13}$-PILC show that a 3.6% mass loss is observed between 100 and 250 °C. Another mass decrease of 2.5% is detected between 250 and 425 °C. A third 3.0% weight loss between 425 and 600 °C is attributed to the completion of the dehydroxylation of the [Al$_{13}$O$_4$(OH)$_{24}$(H$_2$O)$_{12}$]$^{7+}$ ions and montmorillonite layers; Figure 3A.

TGA studies in air of M[(μ-OH)Cu(μ-OCH$_2$CH$_2$NEt$_2$)]$_6$(PF$_6$)$_3$, the reference Cu hexamer hexafluorophosphate salts, indicate that ligand loss occurs in a two-step process between 200 and 330 °C, Figure 3B. Though a two-step decomposition is also observed in the bi-PILC, the pillaring process appears to have broadened the temperature range over which ligand

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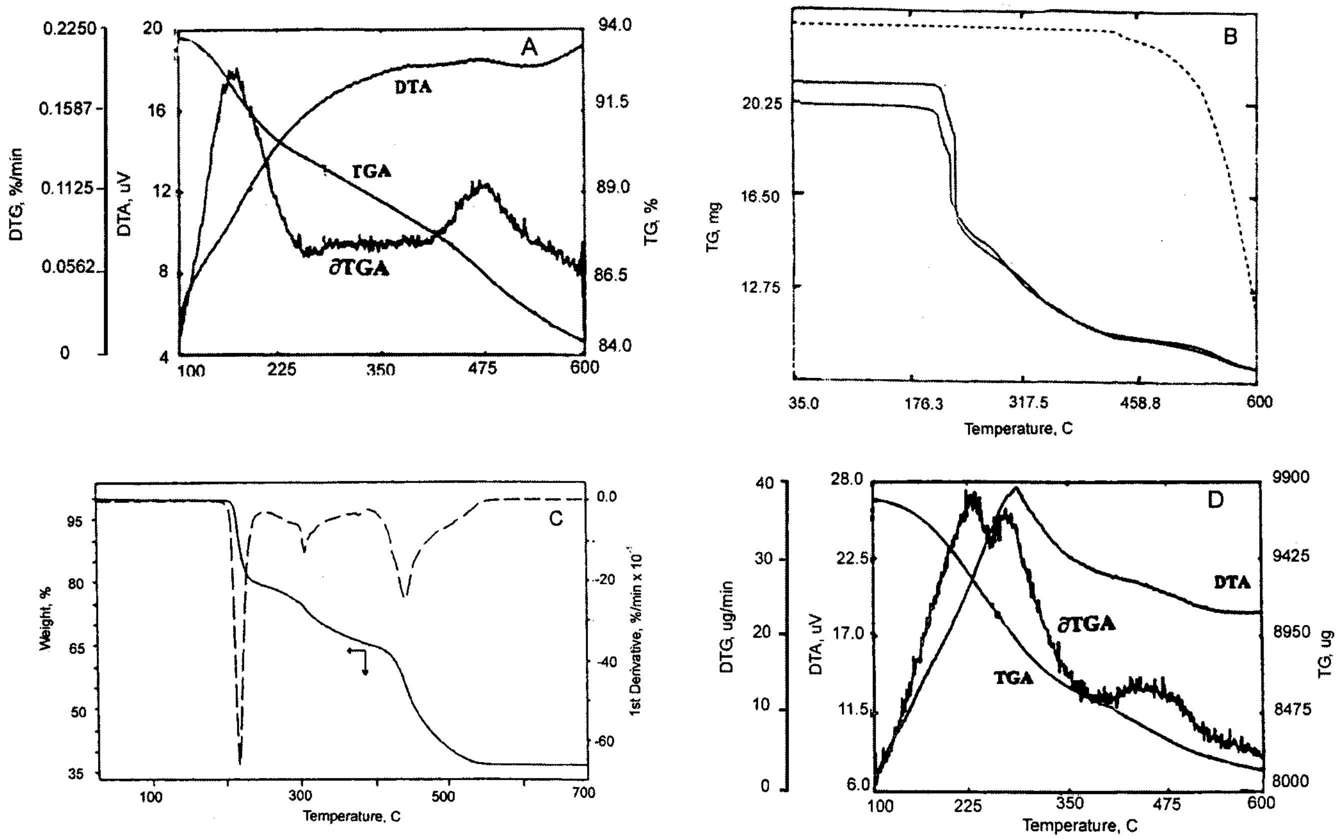

Figure 3. Thermograms in air for (A) the intermediate Al_{13}-PILC, (B) the $M[(\mu\text{-}OH)Cu(\mu\text{-}OCH_2CH_2)NEt_2]_6(PF_6)_3$ where M = Al, Fe salt (the dotted line is for KPF), (C) the $Cr[(\mu\text{-}OCH_3)(\mu\text{-}OCH_2CH_2NEt_2)CuCl]_3$ salt, and (D) the bi-PILC sample containing $Al[(\mu\text{-}OH)Cu(\mu\text{-}OCH_2CH_2\text{-}NEt_2)]_6^{3+}$ ions.

losses occur. Thermogravimetric analysis of the $Cr[(\mu\text{-}OCH_3)(\mu\text{-}OCH_2CH_2NEt_2)CuCl]_3$ salt in Figure 3C shows that this complex decomposes in four steps and that decomposition is complete at 600 °C. The residue has been identified by XRD to consist of a mixture of copper, cupric oxide, and chromium oxide. These oxides could impart unique catalytic properties to the clay microporous structure.

Although the central metal atom affects the complex thermal stability, the decomposition for bi-PILC materials prepared from $M(\mu\text{-}OH)Cu(\mu\text{-}OCH_2CH_2NEt_2]_6(ClO_4)_3$ solutions yields similar thermograms. In Figure 3D**,** the TGA thermogram in air for the bi-PILC containing (Cu,Al) hexamer ions (sample 1, Table 1) exhibits a mass loss of 6.6% prior to 250 °C followed by another 6% decrease from 250 to 390 °C. When the sample is heated in nitrogen, only a 9% mass loss prior to 390 °C is noted. These weight losses have been attributed to the stepwise decomposition of the complex. A final 4.4 wt % loss between 390 and 600 °C is attributed to dehydroxylation reactions.

Surface Area and Pore Volume. Nitrogen porosimetry results for the calcined bi-PILC samples are shown in Table 2. After calcination in air, the oxidative decomposition of the organic components makes the interlayer microporous volume accessible to the nitrogen probe, yielding the surface area values in Table 2. In the 100−500 °C temperature range, all samples suffer structural degradation due to pillar instability.

Bi-PILC containing both Al_{13} clusters and $M[(\mu\text{-}OH)Cu(\mu\text{-}OCH_2CH_2NEt_2)]_6^{3+}$, have surface areas after calcination in air at 500 °C that correlate well with the complex stability as observed by XRD measurements, see Figure 2A−C. In fact, materials containing the least stable (Cu,Fe) hexamer cations have the lowest surface area values and those containing the stable (Cu,Ga) hexamers produce surface areas similar to the one in the parent Al_{13}-PILC. As a result they contain more interlamellar volume than their Al,Cu- or Fe,Cu-containing counterparts; Table 2. Elemental analysis and XRD results indicate that $Fe[(\mu\text{-}OH)Cu(\mu\text{-}OCH_2CH_2NEt_2)]_6^{3+}$ cations undergo partial decomposition during the bipillaring reaction, and the Fe^{3+} thus generated could interact with the Al_{13} clusters in the silicate layers, thus decreasing pillar stability.[17] During calcination at 500 °C, their microporous structures collapse, leaving a residue containing mainly macro- and mesopores; Table 2.

Table 2. Bi-PILC BET Surface Area (m^2/g) and DFT Pore Volumes (cm^3/g) at 500 °C

sample	BET SA	DFT PV <100 nm	<10 nm	<3 nm
1. bent. H	52			
2. Al-PILC	256			
3. AlCu-12	214	0.179	0.0795	0.0427
4. AlCu-13	227	0.165	0.0805	0.0468
5. AlCu-14	204	0.252	0.0977	0.0369
6. AlCu-15	87	0.208	0.0723	0.0109
7. FeCu-3	120	0.180	0.0796	0.0203
8. FeCu-4	116	0.180	0.0860	0.0183
9. FeCu-5	84	0.187	0.0684	0.0099
10. FeCu-6	120	0.295	0.229	0.0000
11. GaCu-1	234	0.310	0.162	0.0835
12. GaCu-2	211	0.211	0.134	0.0596
13. GaCu-3	258	0.217	0.127	0.0553
14. GaCu-4	226	0.232	0.105	0.0444

Typically, Al_{13}-PILC are materials characterized by a long-range stacking of expanded clay platelets connected face-to-face generating microporous aggregates with slitlike pores.[11] Pores in the meso−macroporous region are the results of stacking disorders and of face-to-edge and edge-to-edge connections of contiguous silicate layers or of silicate layer

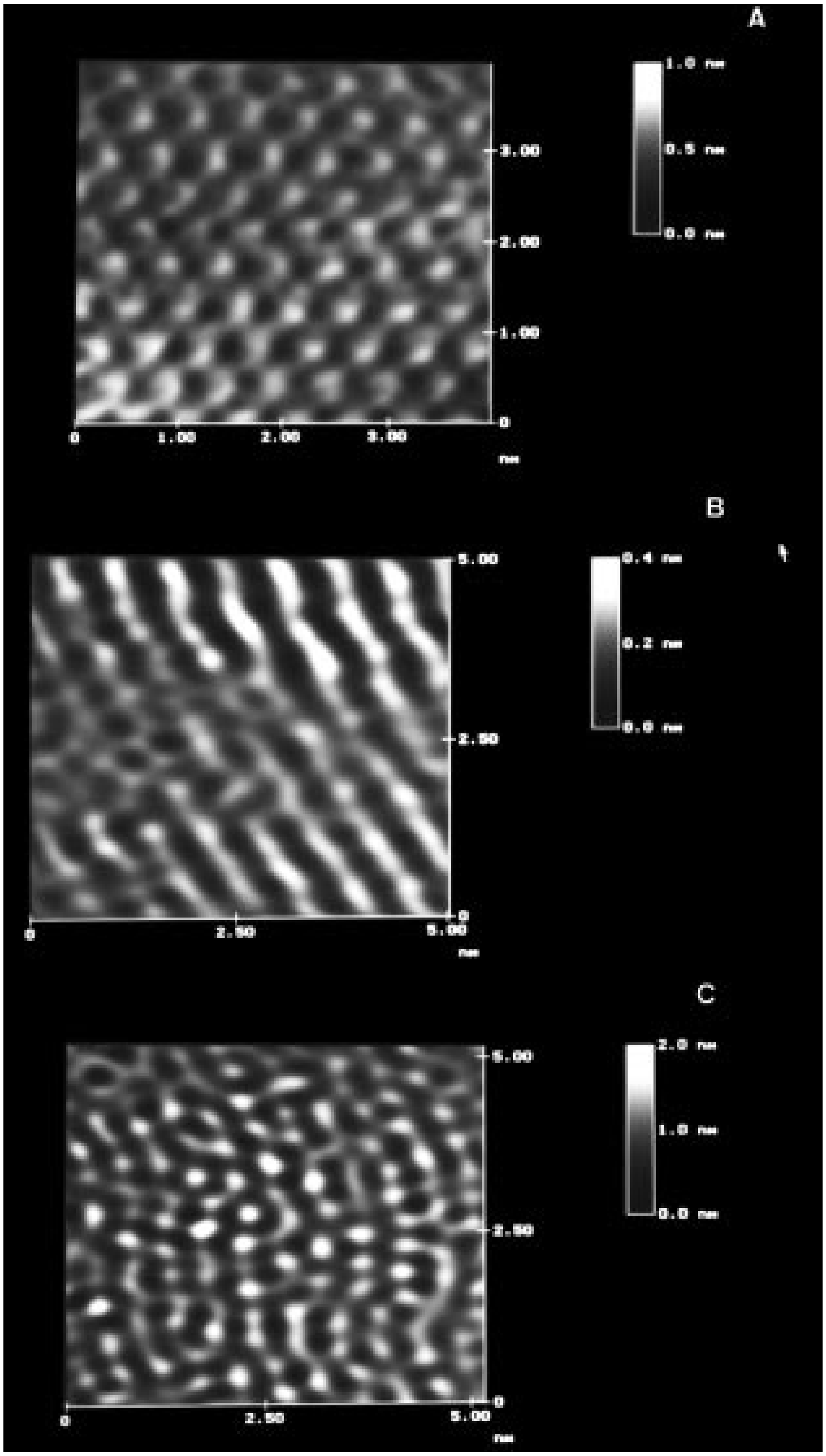

Figure 4. AFM images of (A) the intermediate Al_{13}-PILC and (B) the bi-PILC sample prepared with $Al[(\mu\text{-}OH)Cu(\mu\text{-}OCH_2CH_2NEt_2)]_6^{3+}$ ions at the beginning of the imaging session and (C) at the end of the imaging session.

aggregates.[11] In all the bi-PILC samples examined, the pore volume is mainly in meso- and macropores resulting from intraparticle voids between clay platelet aggregates. The low percentage of pores with $d < 3.0$ nm indicates short-range stacking of clay platelets forming house-of-cards structures. In general, bi-PILC have smaller interlamellar pore volumes than the reference Al_{13}-PILC. This result is attributed to partial layer collapse upon calcination and to the presence of metal oxides in the interlayer region.

AFM Results. The images in Figure 4A were obtained with the same contact mode AFM described in a companion paper[10] and elsewhere.[9] The surface of the reference Al_{13}-PILC, like the parent montmorillonite, is characterized by a hexagonal arrangement of white spots that represent the three basal oxygen atoms of a SiO_4 unit.[8,9] The fourth oxygen points in the direction of the plane and therefore is not visible. Cross-sectional analysis of the surface in the figure has revealed that the next-neighbor distance a between white spots has an average value of 0.53 nm and that the avarage lateral distance l between white spots is 0.93 nm; see Figure 4A. These dimensions are well in agreement with the unit cell size of other pillared bentolite-H samples and with the unit cell dimensions of the parent

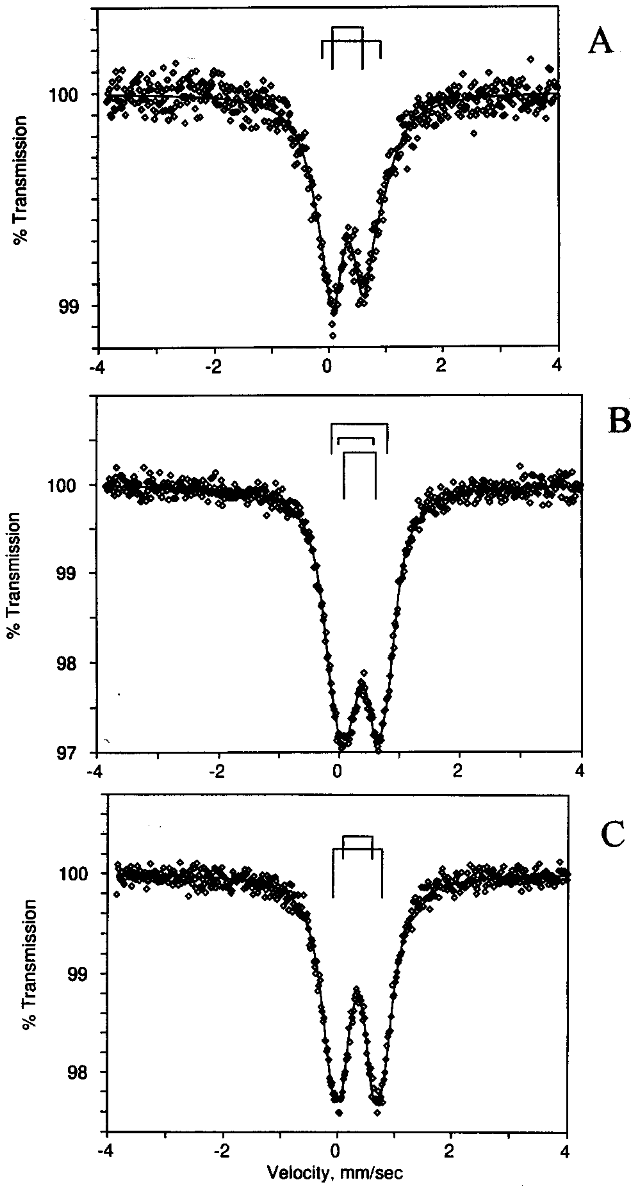

Figure 5. Mossbauer spectra of (A) parent montmorillonite, (B) the Fe[(μ-OH)Cu(μ-OCH$_2$CH$_2$NEt$_2$)]$_6$(ClO$_4$)$_3$ salt, and (C) The bi-PILC sample prepared with Fe[(μ-OH)Cu(μ-OCH$_2$CH$_2$NEt$_2$)]$_6$$^{3+}$ ions.

montmorillonite.[9] At the beginning of the imaging session, it is observed that the typical repeat distances anticipated for the silicate sheet are no longer present and the surface appears to contain adsorbed species generating rows of white spots 0.50 nm apart, Figure 4B. As the imaging session progressed, the surface topography changed completely, Figure 4C. The tip of the cantiliver acts as a molecular broom rearranging the surface distribution of the sorbed hexamer molecules. Thus the hexamer−clay surface interactions are similar to those between Co trimers and montmorillonite,[10] amines, and zeolites, but weaker than those observed between quaternary ammonium cations and zeolites.[19]

Table 3. Mossbauer Results for Air-Dried Samples[a]

sample	isomer shift (mm/s)	quad. split. (mm/s)	Fe (%)	assignment
montmorillonite	0.41	1.03	39	Fe(VI)
	0.34	0.53	61	Fe(VI)
(Cu,Fe) hexamer	0.28	0.59	8	Fe(IV)
	0.34	0.93	36	Fe(VI)
	0.35	0.53	56	Fe(VI)
bi-PILC	0.35	0.51	22	Fe(VI)
	0.35	0.86	78	Fe(VI)

[a] Only Fe^{3+} was detected.

Mossbauer Results. The Texas bentonite sample contains low (<1.0 wt % Fe$_2$O$_3$) iron impurities. The parent montmorillonite Mossbauer spectrum was exceedingly weak; the maximum absorption effect was only about 1%; Figure 5A. However, it is possible to conclude that almost all of the iron in this clay is ferric; Table 3. The overall spectrum is somewhat asymmetric, and this is reflected in the different IS values for the two absorptions. Similar results have been obtained for a different sample of the same clay.[17]

The spectrum of Fe[(μ-OH)Cu(μ-OCH$_2$CH$_2$NEt$_2$)]$_6$(ClO$_4$)$_3$ crystals is also subtly asymmetric; Figure 5B. It could not be fitted adequately with just two doublets, and a small third doublet was necessary to allow for the asymmetry of the spectrum. All of the iron in the material is ferric; Table 3. The two larger doublets have isomer shifts that are more consistent with ferric in octahedral coordination, whereas the significantly lower isomer shift of the smallest doublet is more consistent with tetrahedral coordination. Since it is known that there is only one structural site in the hexamer, the presence of Fe^{IV} is associated with a phase impurity. More likely, it is possible that the hexamer has dehydrated somewhat in time, causing a small fraction of Fe^{IV} sites to have reduced coordination and isomer shift values, see Table 3.

The bi-PILC spectrum is significantly different from those of both the parent montmorillonite and the Fe[(μ-OH)Cu(μ-OCH$_2$CH$_2$NEt$_2$)]$_6$(ClO$_4$)$_3$ crystals, Figure 5C. As in the other materials, all of the iron is present in the ferric oxidation state; however, unlike the other two spectra, the bi-PILC spectrum is virtually symmetric. It was fitted with two doublets with identical isomer shifts, the values of which are more consistent with ferric in octahedral rather than tetrahedral or any other coordination. In contrast to the other spectra, the outer doublet is more intense than the inner doublet, which is why the valley between the peaks is much more pronounced in this spectrum. However, it should be noted that, despite the relative differences in intensity, there is a close correspondence between the Mossbauer parameters for the two doublets for the bi-PILC and those for the two most intense doublets in the Fe[(μ-OH)Cu(μ-OCH$_2$CH$_2$NEt$_2$)]$_6$(ClO$_4$)$_3$ spectrum. In summary: in agreement with chemical analysis data in Table 1, in Fe-containing bi-PILC samples the hexameric complex does not appear to be present in its pristine form.

Discussion and Conclusions

Preexpanding clay minerals with molecules intended to be replaced by different intercalants is an established practice.[20] Wedging agents are frequently employed when the desired pillar does not possess sufficient charge density to penetrate the interlamellar region.[20] Though such preintercalants are normally polar molecules possessing long alkyl chains, in this research, Keggin ions [Al$_{13}$O$_4$(OH)$_{24}$(H$_2$O)$_{12}$]$^{7+}$ were used as wedging agents. A similar approach[2] has been used to prepare Al-PILC containing [Co$_3$(OC$_2$H$_4$NH$_2$)$_6$]$^{3+}$ ions.

Though the identity of the central metal varies, the structures of all three cationic Cu complexes are virtually identical. By

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reacting an Al_{13}-PILC with these complexes it is possible to replace some of the Al species in the expanded clay with hexameric ions and introduce into the Al_{13}-PILC microstructure metals such as Fe, Cu, and Ga that could impart to these microporous solids unique catalytic properties. In all the samples examined, molecular scale AFM images have shown that hexamer molecules are also adsorbed on the clay outer surface.

Bi-PILC containing $[Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{7+}$ as well as $M[(\mu\text{-OH})Cu(\mu\text{-OCH}_2CH_2NEt_2)]_6{}^{3+}$ ions are microporous materials whose stability and microporosity depend mainly on the identity of the hexamer central metal atom. Stability increases in the order Fe < Al < Ga.

The thermogravimetric decompositional sequence does not appear to vary for this isostructural series of complexes. Total ligand decomposition is achieved by 330 °C regardless of the identity of the central metal ion.

Although none of the complexes exhibited any sign of instability even after lengthy heating in acetonitrile, elemental analysis together with XRD data indicate that the bi-PILC synthesis procedure may decompose these hexamers in part. The presence of residual water molecules in the clay interlamellar space could have hydrolyzed the hexameric ions. Interaction of these decomposition products with the Al_{13} pillars destabilizes the Keggin ion structure.[17] The $[Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{7+}$ ion [21] consists of 12 Al^{VI} atoms surrounding a central Al^{IV} believed to be available to exchange.[16,17] Replacement of the central Al^{IV} atoms with Fe^{3+} has been observed to decrease the bi-PILC stability.[17] Thus the decreased thermal stability of the bi-PILC materials could be the result of interactions between the Keggin ions and metals such as Fe^{3+} and Cu^{2+}.

The wide range of isomer shifts and quadrupole splittings, observed for the parent clay and its iron impurities, precludes the unequivocal assignment of the observed Fe^{3+} to the clay or to the hexamer complex sandwiched between the clay silicate layers. The Mossbauer parameters for the largest Fe^{3+} absorption for the parent clay and for the (Cu,Fe)-hexamer do not deviate significantly from each other, Table 3. Therefore the corresponding minor doublet in Figure 5C for the bi-PILC spectrum could arise from the clay Fe impurities or from the hexamer complex. However, the bi-PILC spectrum major doublet in Figure 5C appears to be more compatible with the minor doublet observed in the hexamer spectrum in Figure 5B and much less so with the second doublet in the parent montmorillonite; see Figure 5A. These results alone are not sufficient to assign the Fe to residual hexamer pillars, and additional corroborative evidence is needed.

The neutral trimeric chromium $Cr[\mu\text{-OCH}_2CH_2NEt_2CuCl]_3$ consists of three copper atoms chelated with a central, coordinatively saturated chromium, connected to each copper through two bridging alkoxides. This complex can be occluded in the Al_{13}-PILC microspace to form Cr-containing bi-PILC materials as stable as the parent material. The trimeric chromium complex appears to undergo partial decomposition at temperatures <500 °C when dehydroxylation of the clay layers occurs. This high decomposition temperature suggests that interactions of the Cr complex with the Al pillars are negligible.

In summary, stable microporous materials, with surface areas in the 200−260 m^2/g range and containing mixtures of chromium oxides, or mixtures of copper, gallium, and iron oxides, have been synthesized. Heat stable Al_{13}-PILC promoted with chromium oxides could find application as catalysts in a variety of technologically important reactions that include hydrogenation and dehydrogenation of hydrocarbons, dehydrocyclization of paraffins, dehydroisomerization of paraffins, olefins and naphthenes, and the polymerization of olefins.[22−24] In contrast, copper-containing Al_{13}-PILC could join the family of copper-promoted microporous catalysts for NO decomposition and for the selective reduction of nitrogen oxides.[25−27]

Safety Note

CAUTION. The perchlorate salts used are potentially explosive and are particularly unstable when exposed to a heat source. All perchlorate salts should be handled with great caution [Cf.: *J. Chem. Educ.* **1973**, *50*, A335; *Chem. Eng. News* **1983**, *61* (Dec 5) 4; **1963**, *41* (July), 47].

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