

as a combination of coordinatively unsaturated Mo(VI) and Mo(IV) fragments presumably through Mo=O→Mo interaction. This view may be supported by the observation that MoO₂-(OSiMe₂(*t*-Bu))₂(py)₂ was obtained as a colorless crystalline solid from Mo₃O₆(OSiMe₂(*t*-Bu))₄(py)₃.

The cocondensation reaction of Me₃SiOPh with MoO₃ appears to be far simpler with the crude reaction product showing, by ¹H NMR spectroscopy, MoO₂(OPh)₂ and (Me₃Si)₂O with only trace amounts of other contaminants. This shows phenoxide to have a stronger affinity for the Mo(VI) center than does the trimethylsiloxy group. Furthermore, the reaction is enhanced by the formation of a good leaving group, i.e., hexamethyldisiloxane.

The cocondensation reaction of Me₃SiOMe with MoO₃ is expected to give MoO₂(OSiMe₃)(OMe) along with the symmetric products MoO₂(OMe)₂ and MoO₂(OSiMe₃)₂.

Mass spectral data for the crude product indeed show the possible monomeric fragment ions, which indicates both methoxy and siloxy groups are actually incorporated in the condensate. The ¹H NMR spectrum of the crude product in pyridine-*d*₅ shows very broad methoxy peaks at 4.5 (fwhh = 12.8 Hz) and 5.0 ppm along with two broad siloxy peaks at 0.26 and 0.33 ppm. The broadness of the peaks suggests that the compound does not dissociate totally even in pyridine, a powerful coordinating agent. The total ratio of groups between MeO and Me₃SiO in the crude solid is approximately 2, which indicates more methoxy groups are incorporated in the crude product and is consistent with the observation that hexamethyldisiloxane was formed from the cocondensation reaction, as indicated by ¹H NMR spectroscopy and GC/MS. Attempts to purify the compound by vacuum sublimation were unsuccessful. Most of the product decomposed to give a blue molybdenum oxide residue and volatiles along with a trace amount (approximately 1% by weight) of a white solid. The ¹H NMR spectrum of this white sublimate in pyridine-*d*₅ shows more siloxy groups relative to methoxy groups (the ratio is 1.6). This suggests that the dioxodisiloxymolybdenum(VI) fragment is more volatile than the methoxy counterpart and that the stoichiometric dioxomethoxysiloxymolybdenum(VI) compound could not be obtained by sublimation.

It is interesting to note that the MoO₂(OSiMe₃)(OMe) product is much less thermally stable than MoO₂(OMe)₂. Easy formation of hexamethyldisiloxane without reduction is probably one of the reasons. The solution decomposition is particularly facile, giving primarily starting ligand and presumably MoO₃ as a white precipitate. The thermal decomposition in the solid state (363 K,

1 × 10⁻⁴ Torr) gives starting ligand (26 mol %), hexamethyldisiloxane (22 mol %), methanol (42 mol %), dimethoxymethane (9 mol %), methyl formate (2 mol %), formaldehyde (trace), and dimethyl ether (trace). It is interesting to note that the solid-state decomposition shows a diverse product distribution compared to that of the solution decomposition. Apparently, the presence of excess methoxy groups accompanied by the ease of reduction of the Mo=O moiety at elevated temperature accounts for this discrepancy.

The cocondensation reaction of Me₂Si(OMe)₂ with MoO₃ was studied. Reaction readily occurs on warming to room temperature. The ¹H NMR spectrum of the crude material in benzene-*d*₆ gave a complex series of resonances in the methoxy region, from 3.3 to 3.5 ppm (methoxy bonded to Si) and from 4.0 to 4.7 ppm (methoxy bonded to Mo), and in the alkylsiloxy region, from 0.2 to 0.5 ppm. This indicates the formation of many products involving Mo-OMe and Mo-O-Si units. Of interest is that volatiles from thermal decomposition of the crude product were shown to be primarily starting material, Me₂Si(OMe)₂ rather than oxidized products of the methoxy ligand as was observed for the thermal decomposition of the product from the reaction of Me₃SiOMe and MoO₃. This may be ascribed to the inability to form disiloxane by the Me₂Si group in a localized environment.

¹H NMR data of all of the compounds (except pyridine adducts) studied here show them to be polymeric in noncoordinating solvents. Pyridine serves as an excellent coordinating agent, and solvent, and breaks down the polymers in solution for all except MoO₂(OMe)₂ and the nonstoichiometric crude products from the MoO₃/Me₃SiOMe and the MoO₃/Me₂Si(OMe)₂ systems, which still display polymeric behavior in pyridine. A dramatic change in the ¹H NMR spectrum is shown in Figure 1, for which the addition of 2 equiv or more of coordinating agent to a benzene solution of MoO₂(OEt)₂ gives the characteristic sharp ethoxy resonances.

It is interesting to note that, while Chisholm et al. have isolated MoO₂(O-*t*-Bu)₂, we were unable to prepare this compound by the cocondensation reaction of MoO₃ with Me₃SiO-*t*-Bu. In this case the reaction products of isobutene and *tert*-butyl alcohol indicate catalytic H abstraction by the Mo=O moiety occurs extensively for the *tert*-butyl group, presumably due to the proximity of hydrogen atoms of *tert*-butyl groups to the oxygen of MoO₃.

Cocondensation reactions of MoO₃ with nitrogen-containing organosilanes and cluster syntheses employing MoO₂(OR)₂ compounds via reduction processes are in progress.

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Pillaring of Layered Titanates by Polyoxo Cations of Aluminum

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Layered tetratitanate complexes pillared with [Al₁₃O₄(OH)₂₄(H₂O)₁₂]⁷⁺ Keggin ions have been prepared through a stepwise exchange process. The exchange of the large polyoxo cations of aluminum was facilitated by the opened layers of alkylamine-intercalated complexes. The stability of the interlayer alkylammonium ions played an important role in holding the interlayer spacing during the exchange process. Alkylamines were used instead of inorganic bases to hydrolyze aluminum chloride solutions. This effectively excluded any other cations from competing for the ion-exchange sites on the tetratitanate complexes. The best sample was obtained by exchanging a hexylammonium tetratitanate complex in a hexylamine-hydrolyzed AlCl₃ solution at 50 °C for 8 h. The physical properties of the resultant pillared complexes were characterized with respect to their thermal stability and porosity.

Introduction

The intercalation of layered metal oxides with polar organic molecules is long established and well documented. Barrer and MacLeod¹ demonstrated in 1955 that porosity can be introduced

in smectite clays by ion-exchanging tetraalkylammonium ions between the silicate layers. The sorptive properties of these intercalated materials were reviewed by Barrer² in 1978. Organic molecules have also been reported to be weakly bound in the

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interlayers of crystalline silicic acids such as phyllosilicic acid and H-magadiite.^{3,4} Of interest here is that such intercalation chemistry is not limited to the silicate families that are based on tetrahedral framework structures. A series of layered titanates and titanoniobates based on octahedral framework structures also incorporate amines to form intercalated derivatives.^{5,6} Research in this field has been attractive to a number of scientists because of its potential in separations, sorption, mineralogy, and catalysis. The main shortcoming of these organic intercalated materials for application as catalysts in high-temperature processes is their insufficient thermal stability. Thermostable molecular sieve like structures have been developed by interaction of smectite clay minerals with inorganic cross-linking agents, such as aluminum hydroxide oligomers,^{7,8} and tetrameric hydroxyzirconium cations.⁹ These pillared clays, exposing their interior surface areas for catalytic reactions and by showing zeolitic properties, have demonstrated remarkable activities in cracking and esterification processes.^{10,11} Because smectite clays are capable of swelling and expand in aqueous solutions, pillared clays are usually synthesized by reacting an aqueous solution of inorganic oligomers with a unit-layer dispersion of smectite clays.⁷ Similar processes, however, are not applicable to families of layered metal oxides that possess a high charge density on the framework. To the best of our knowledge, smectite clays have been the only layered materials reported up to now that can be pillared with inorganic cross-linking agents and form molecular sieve structures.

Titania has several significant and distinctive properties as a catalyst support. TiO_2 is easily reduced to form various stoichiometric and nonstoichiometric lower oxides. The strong-metal-support interaction (SMSI) was first reported for noble metals supported on TiO_2 .¹² In the 1970s a TiO_2 -based catalyst was first applied commercially in air pollution control equipment and was found to be the best catalyst for the selective catalytic reduction of NO_x (NO and NO_2) with NH_3 (SCR process).¹³ TiO_2 -based catalysts, therefore, became an attractive subject of many scientific studies.¹⁴ However, compared to Al_2O_3 and SiO_2 , TiO_2 has weaker acidity and relatively lower surface area. In order to increase the surface areas of titania-based catalysts, the approach in this work is to pop open the layered titanates with the inorganic Keggin ions, $[\text{Al}_{13}\text{O}_4(\text{OH})_{24}(\text{H}_2\text{O})_{12}]^{7+}$. Methods applied were not quite similar to those used previously for pillar clays. Unlike clays, layered titanates do not swell in water. Amines readily intercalate and increase the interlayer distance to almost any required level.⁵ The opened layers then facilitate the replacement of RNH_3^+ ions by the large inorganic cations. Similar techniques have recently been applied to the layered compounds of zirconium and titanium phosphates.¹⁵ In the tetratitanate system, however, the exchange processes are very much affected by other competing cations in the solutions. Detailed studies in the exchange processes were carried out, followed by a brief characterization of the resultant materials.

Experimental Section

Reagents. Reagent grade chemicals were used without further purification. TiO_2 (anatase), K_2CO_3 , and pyridine were purchased from Merck. HCl , $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$, *n*-butylamine, and *n*-hexylamine were from Riedel-deHaen.

Synthesis of Layered Tetratitanates. $\text{K}_2\text{Ti}_4\text{O}_9$. The named compound

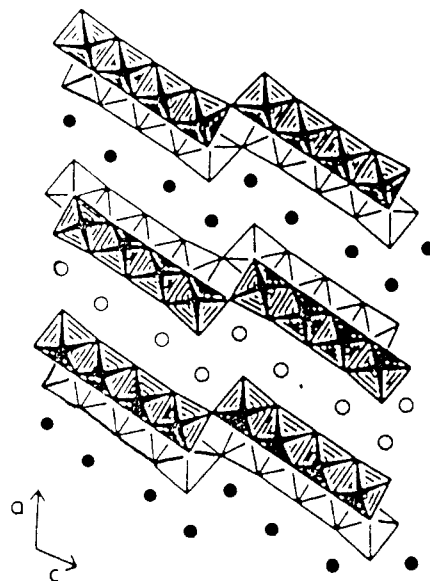


Figure 1. Idealized representation of the crystal structure of $\text{K}_2\text{Ti}_4\text{O}_9$ projected along (010): \circ , K^+ ions at the level $y = 1/4$; \bullet , K^+ ions at $y = 3/4$.

was obtained by a solid-state reaction of a stoichiometric mixture of TiO_2 and K_2CO_3 powder. These were dehydrated at 100°C for 5 h before being ground and well mixed in air. After 20 h of heating at 800°C , the product was identified by X-ray powder diffraction techniques. The hydrated derivative, $\text{K}_2\text{Ti}_4\text{O}_9 \cdot \gamma\text{H}_2\text{O}$, was prepared by refluxing 0.5 g of $\text{K}_2\text{Ti}_4\text{O}_9$ powder in 100 mL of 0.1 M KOH solution for 20 h.

$\text{H}_2\text{Ti}_4\text{O}_9 \cdot x\text{H}_2\text{O}$. One gram of $\text{K}_2\text{Ti}_4\text{O}_9$ powder was stirred in 20 mL of HCl solution for 6 h. The concentration of the acid was varied from 0.05 to 1 M in order to find the proper exchange condition. The effect of exchange temperature was also examined.

***n*-Butylammonium and *n*-Hexylammonium Tetratitanates.** Ion-exchange behavior of $\text{K}_2\text{Ti}_4\text{O}_9$, $\text{K}_2\text{Ti}_4\text{O}_9 \cdot \gamma\text{H}_2\text{O}$, and $\text{H}_2\text{Ti}_4\text{O}_9$ was studied. Four grams of each was stirred with 500 mL of ca. 5 M *n*-butylamine or *n*-hexylamine solution for 7 days, followed by filtering and washing with deionized water.

$[\text{Al}_{13}\text{O}_4(\text{OH})_{24}(\text{H}_2\text{O})_{12}](\text{Ti}_4\text{O}_9)_7$. Alkylammonium tetratitanate powder was reacted with base-hydrolyzed aluminum chloride solutions. The optimum exchange amount was investigated as a function of temperature and reaction period. The base used for hydrolyzing aluminum chloride solution was found to be one of the key factors in determining the structures of the products.

Preparation of Solutions Containing $[\text{Al}_{13}\text{O}_4(\text{OH})_{24}(\text{H}_2\text{O})_{12}]^{7+}$ (Al_{13}^{7+}) Keggin Ions. The base solution was added dropwise to AlCl_3 solution with vigorous stirring. The base/Al mole ratio was 2.5, and the final pH value was adjusted to 4–4.5. The formation of Al_{13}^{7+} Keggin ions was confirmed by ^{27}Al NMR spectra.

Apparatus. X-ray powder diffraction patterns were obtained by using a Phillips 1792 X-ray diffractometer and $\text{Cu K}\alpha$ radiation. Infrared spectra were obtained with a Perkin-Elmer 983 spectrometer. ^{27}Al NMR spectra were obtained with a Bruker AM-300WB NMR spectrometer. Thermogravimetric analysis was carried out with a Du Pont 951 thermogravimetric analyzer programmed for a heating rate of $10^\circ\text{C}/\text{min}$ under a nitrogen atmosphere. The concentrations of pillar polyoxo cations of aluminum were determined on the calcined samples with a Perkin-Elmer 5000 atomic absorption spectrophotometer. The measurement of the surface areas and pore size distribution of the catalysts was based on the physical adsorption of nitrogen at liquid N_2 temperature determined by using a volumetric system.

Results and Discussion

The sheet structure of potassium tetratitanate, which serves as starting material in this work, is depicted in Figure 1 according to Dion et al.¹⁶ The basic framework is built of four octahedra sharing edges at one level that combine with similar units above and below to form zigzag ribbons of octahedra.

The extent of proton exchange for interlayer K^+ ions in $\text{K}_2\text{Ti}_4\text{O}_9$ in HCl solutions was found to be a function of temperature and

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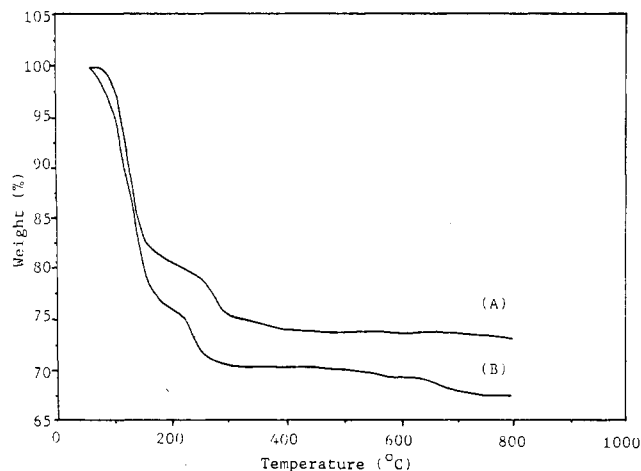
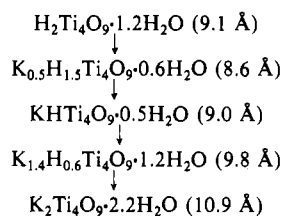


Figure 2. TGA curves of (A) butylammonium tetratitanate and (B) hexylammonium tetratitanate.

HCl concentration. The reverse process, examined by Sasaki et al.,¹⁷ is a four-stage process:



where the numbers in parentheses indicate the interlayer distance. When 0.05 and 0.1 N HCl solutions were used to exchange K^+ ions between the layers of $\text{K}_2\text{Ti}_4\text{O}_9$, the XRD patterns of the resultant compounds displayed two interlayer distances of 9.2 and 10.4 Å. By comparison with the results of Sasaki et al., the former corresponds to a phase of >50% exchange, while the latter may be a solvated potassium phase with negligible ion exchange. With 1 N HCl solution, on the other hand, 75% of K^+ ions were exchanged by H^+ ions and an interlayer distance of 8.7 Å was observed by XRD techniques. Furthermore, nearly complete exchange was achieved by using 1 N HCl solution and stirring at 70 °C for 6 h. The product has an interlayer distance of 9.1 Å, which is consistent with a composition of $\text{H}_2\text{Ti}_4\text{O}_9 \cdot 1.2\text{H}_2\text{O}$.¹⁷

Formation of alkylammonium tetratitanate complexes was carried out with the proton form of tetratitanate. Consistent with the proposal given by Izawa et al.⁵ that a combination of intercalation and ion-exchange processes was responsible for the formation of the alkylammonium tetratitanate complexes, we found that interlayer H^+ ions were essential for the amine intercalation reaction. The butylammonium tetratitanate complex of 18-Å interlayer distance was obtained either from $\text{H}_2\text{Ti}_4\text{O}_9 \cdot y\text{H}_2\text{O}$ or from partially H^+ -exchanged $\text{K}_2\text{Ti}_4\text{O}_9$ as starting material.

The *n*-hexylammonium tetratitanate complex was prepared according to a similar mechanism. The interlayer distance is 21.6 Å and increases with a gradient of 1.6 Å/carbon number. Since alkyl chains grow by 1.27 Å per added carbon, the gradient suggests that the interlayer alkylammonium ions form double layers with $-\text{NH}_3^+$ groups pointing toward the basal layers. The inclination angle of the alkyl chains to the basal plane is $\approx 39^\circ$, calculated as $\sin^{-1} [1.6 / (2 \times 1.27)]$. This value is much smaller than 57° obtained by Izawa et al.⁵ The amount of alkylammonium ions accommodated between the layers was estimated from thermogravimetric analysis. Both butylammonium and hexylammonium complexes show obvious weight losses in two stages (Figure 2). The butylammonium complex has weight losses of 18% and 5% in the temperature ranges 60–220 and 220–320 °C, respectively. The hexylammonium complex has weight losses of 23% and 6% in the temperature ranges 60–200 and 200–280 °C,

respectively. The weight loss in the lower temperature range corresponds to the desorption of hydrating water molecules, while that in the higher temperature range is considered due to the decomposition of alkylammonium ions. Theoretical values for losing alkylamines in $(n\text{-BuNH}_3)_2\text{Ti}_4\text{O}_9$ and $(n\text{-HexNH}_3)_2\text{Ti}_4\text{O}_9$ complexes are 30% and 37%, respectively. Consequently, only one-sixth of the exchange sites were accommodated by alkylammonium ions.

The decomposition processes of alkylammonium tetratitanates were examined via XRD and IR techniques. Figure 3 demonstrates the structural changes of the hexylammonium complex after heat treatment. The interlayer hexylammonium ions are retained and the basal spacing is kept at ca. 21 Å after the sample is heated at 100 °C for 4 h. After it is heated at 300 °C, the IR absorption peaks at 1400–1550 and 2900 cm^{-1} (corresponding to N–H, C–H bending and C–H stretching vibration modes, respectively) are missing, and the interlayer distance is decreased to ca. 9.1 Å. Further heat treatment at 500 °C for 4 h induces the formation of anatase TiO_2 . On the other hand, the XRD patterns of the butylammonium complex show a shrinking of the interlayer distance from 18.4 to 10.2 Å after heating at only 100 °C, although the IR spectra still reveal peaks from N–H, C–H, and C–N vibration modes (Figure 4). This evidence indicates that the interlayer spacing is collapsed, with the alkyl chains of butylammonium ions lying almost parallel to the basal planes. It is concluded that interlayer butylammonium ions are not as thermally stable as hexylammonium ions with respect to maintaining the interlayer distances of tetratitanates.

Exchange of alkylammonium ions with Al_{13}^{7+} Keggin ions was investigated with both butyl- and hexylammoniumtetratitanates. With NaOH as the base for hydrolyzing AlCl_3 , both compounds collapse to 11.1 Å after reaction. When studying the Na^+/H^+ exchange process on layered titanates, Sasaki et al.¹⁷ reported an interlayer distance of 11.2 Å for compounds of composition $\text{Na}_x\text{H}_{2-x}\text{Ti}_4\text{O}_9 \cdot 3.3\text{H}_2\text{O}$, where *x* ranges from 1 to 1.4. Judging from the similarity of the distance, it is concluded that Na^+ ions existing in the hydrolyzed AlCl_3 solution have competed for the exchange sites between the layers and led to the formation of Na^+ -exchanged tetratitanate.

In order to avoid the interference from other cations in the AlCl_3 solution, alkylamines were used as the base for hydrolysis. The formation of Al_{13}^{7+} ions was confirmed by examining the ²⁷Al NMR spectra of the base-hydrolyzed AlCl_3 solutions (Figure 5). In the absence of added base, the spectrum consists of a single sharp line at 0.0 ppm (Figure 5A), which served as an external reference peak in the following experiment. As NaOH is added, a new sharp line appears at 62.8 ppm. In contrast, with either butylamine or hexylamine as base to hydrolyze AlCl_3 solutions, the only peak observed in the ²⁷Al NMR spectra is that at 62.8 ppm. Akitt et al.^{18–21} have carried out a series of studies on the hydrolysis of aluminum salts in solutions with inorganic bases using ²⁷Al and ¹H NMR results accompanied by X-ray data. They have assigned the sharp line at 0.0 ppm to the $\text{Al}(\text{H}_2\text{O})_6^{3+}$ monomer and the peak at 62.8 ppm to the tetrahedral center of the Al_{13}^{7+} Keggin ions. Therefore, alkylamines are found to be an effective base in hydrolyzing AlCl_3 to form Al_{13}^{7+} Keggin ions in solution.

Exchange of interlayer alkylammonium ions with Al_{13}^{7+} Keggin ions was found to be a function of the thermal stability of the accommodated alkylammonium ions. When the less thermally stable butylammonium tetratitanate is exposed to Al_{13}^{7+} , the interlayer distance decreases from 18.4 to 10.8 Å (Figure 6a). On the other hand, the interlayer distance is retained at 21.6 Å after hexylammonium tetratitanate is stirred with hexylamine-hydrolyzed AlCl_3 solution for a period of up to 5 days. However, if the hexylammonium complex is stirred with butylamine-hydrolyzed AlCl_3 solution at room temperature (Figure 6b), the interlayer distance decreases gradually with time to 16 Å. These

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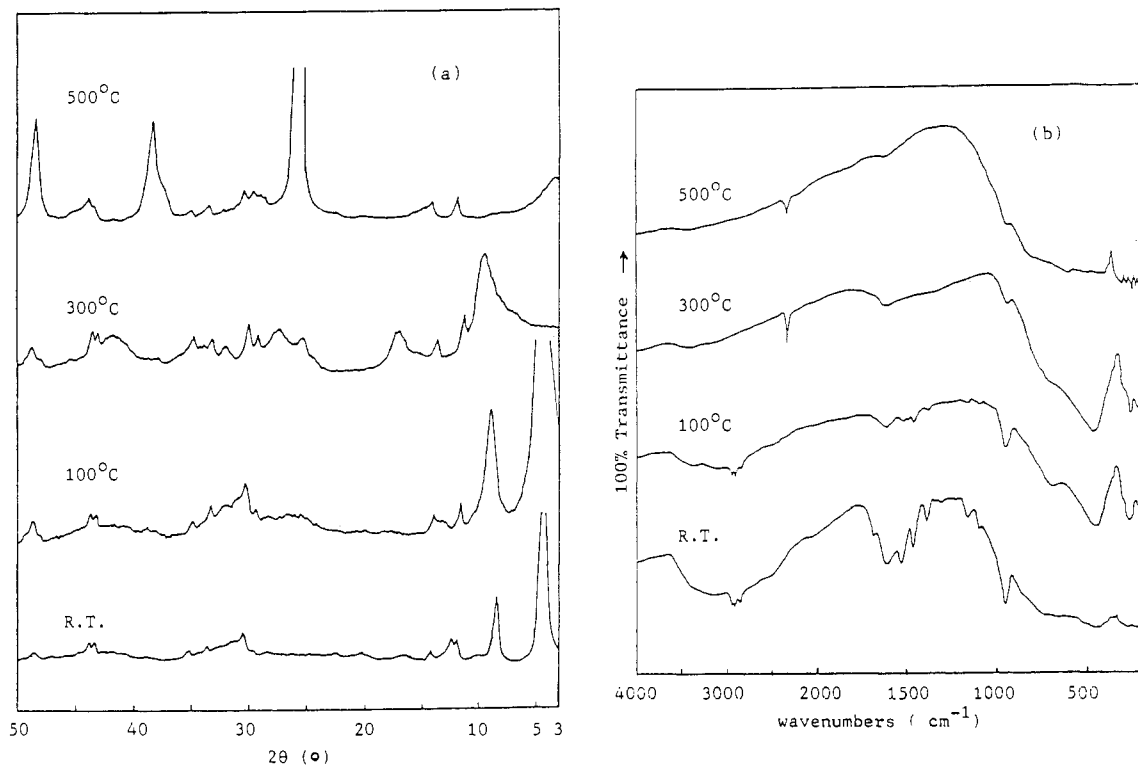


Figure 3. (a) XRD patterns and (b) IR spectra of hexylammonium tetratitanate samples after heating at different temperatures.

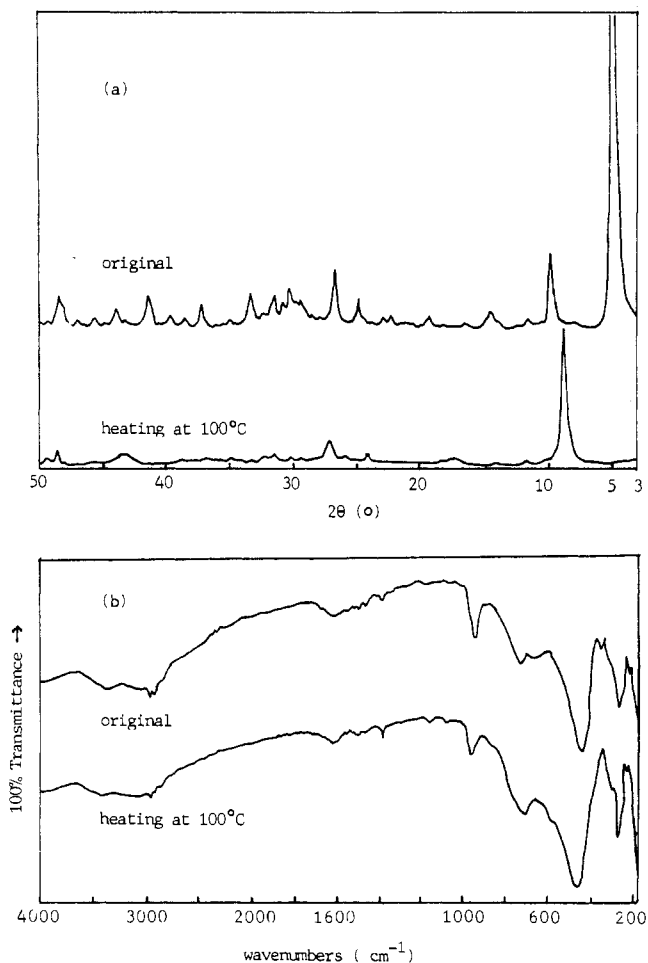


Figure 4. (a) XRD patterns and (b) IR spectra of butylammonium tetratitanate samples before and after heating at 100 °C.

results imply that the low stability of interlayer butylammonium ions is responsible for the collapse of the interlayer spacing. Hexylammonium tetratitanate reacted with hexylamine-hydrated

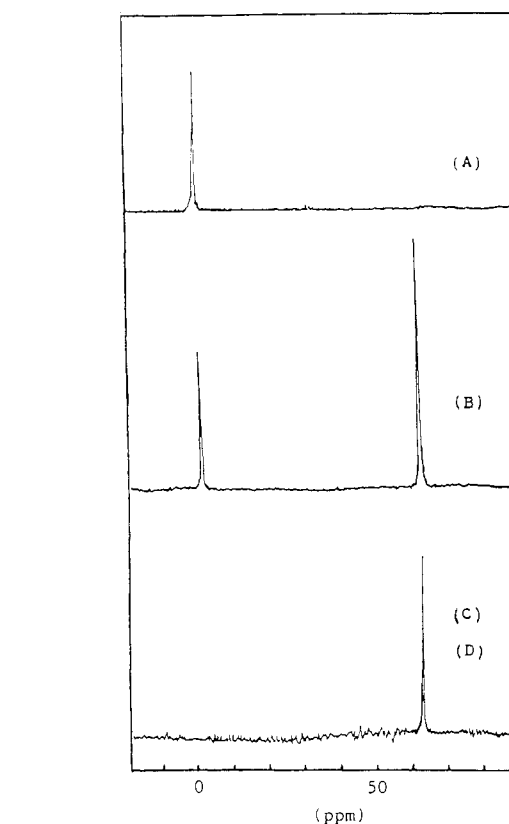


Figure 5. ^{27}Al NMR spectra of AlCl_3 solutions: (A) external reference peak from the signal of $\text{Al}(\text{H}_2\text{O})_6^{3+}$; (B) NaOH-hydrolyzed, (C) *n*-BuNH₂-hydrolyzed, and (D) *n*-HexNH₂-hydrolyzed solutions.

AlCl_3 solution resulted in the best material and was used for all following experiments.

The effect of exchange temperature and reaction period was examined. Conditions are indicated by AT/X/Y/Z, where AT = amine tetratitanate, X = exchange temperature, Y = reaction time, and Z = calcination temperature. The XRD patterns of samples obtained by stirring hexylammonium tetratitanate in

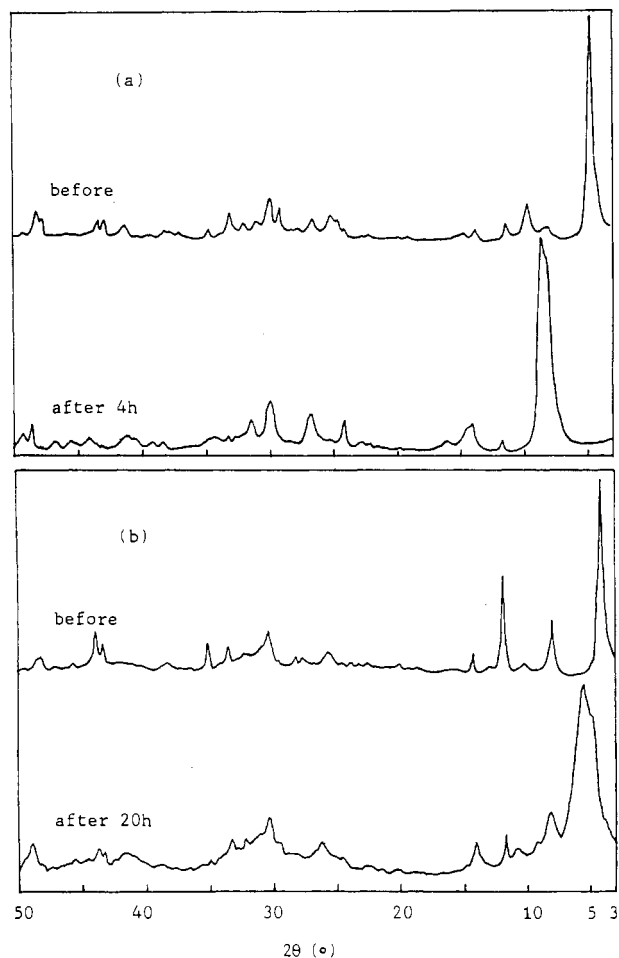


Figure 6. XRD patterns of (a) butylammonium tetratitanate and (b) hexylammonium tetratitanate before and after reacting with BuNH_2 -hydrolyzed AlCl_3 solution.

Table I. Elemental Analysis of Al, Ti, and K Contents in Al_{13}^{7+} -Pillared Samples

sample	ppm			% of exchange sites occupied by Al_{13}^{7+}
	Al	Ti	K	
AT/25/120/500	15.2	50	7.4	57
AT/50/8/500	15.3	40	1.1	72
AT/60/12/500	20.3	42	2.1	93
AT/70/7/500	19.0	40	1.0	91
AT/100/6/500	25.5	28	0.9	170

hexylamine-hydrolyzed AlCl_3 solution for various periods of time at room temperature illustrate that the interlayer distance is retained at ca. 21.6 Å ($2\theta = 4.1^\circ$). This indicates that the interlayer spacings of tetratitanate complexes are still held open by hexylammonium ions, although the crystallinity decreases to some extent after long reaction periods (5 days). After calcination at 500 °C, sample AT/25/120/500 shows that peak at $2\theta = 4.1^\circ$ disappears and a weak peak appears at $2\theta = 5.7^\circ$ (15.3 Å). Rausch and Bale²² have determined the radius of Al_{13}^{7+} ions to be 4.3 Å by small-angle scattering; this agrees well with the theoretically calculated radius from Johansson's data.²³ The thickness of basal Ti_4O_9 layers can be estimated by subtracting the diameter of K^+ ions (3.0 Å) from the interlayer distance of $\text{K}_2\text{Ti}_4\text{O}_9$ (8.7 Å), and a value of 5.7 Å is obtained. Accordingly, the Al_{13}^{7+} pillared tetratitanate should have an interlayer distance around 15 Å. Therefore, the small peak at $2\theta = 5.7^\circ$ ($d = 15.3$ Å) of the calcined sample indicates that Al_{13}^{7+} Keggin ions have been exchanged between the layers.

Figure 7 shows the XRD patterns of Al_{13}^{7+} -exchanged samples obtained at elevated temperatures. All the samples before cal-

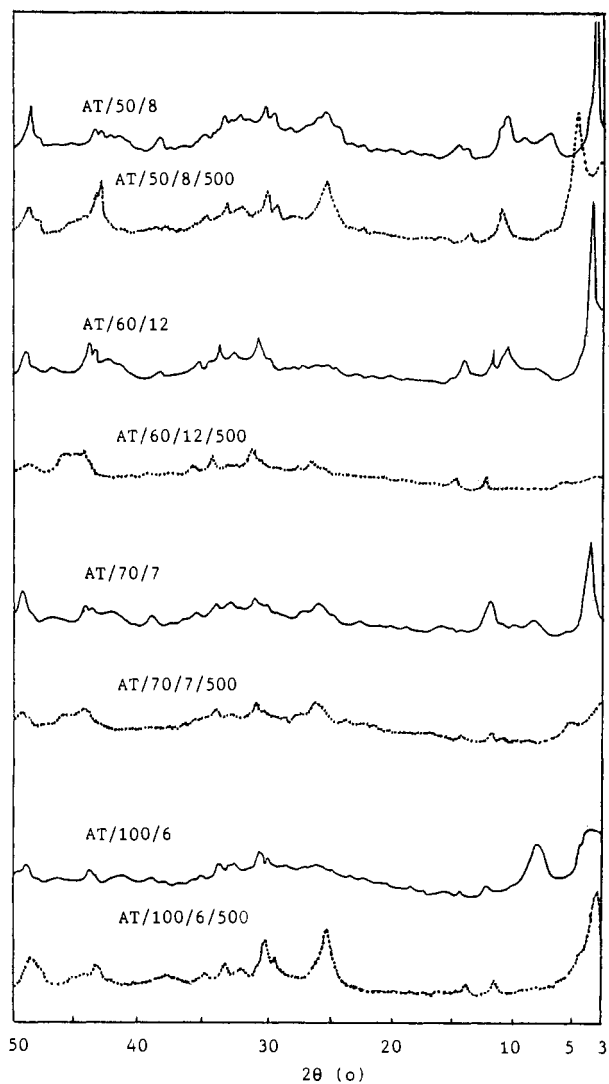


Figure 7. XRD patterns of hexylammonium tetratitanate samples after treatment with HexNH_2 -hydrolyzed AlCl_3 solution at elevated temperatures, before (solid curves) and after (dotted curves) calcination.

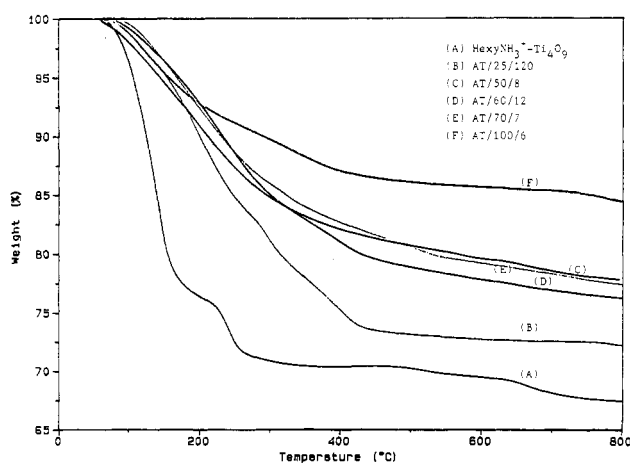


Figure 8. TGA curves of hexylammonium tetratitanate samples before and after pillaring with Al_{13}^{7+} Keggin ions at various temperatures.

ination have the peak at $2\theta = 4.1^\circ$ ($d = 21.6$ Å). However, a decrease in crystallinity is found as the intensity of this peak decreases with the raising of exchange temperature from 50 up to 100 °C. Similar to the phenomena mentioned previously, the peak at $2\theta = 4.1^\circ$ disappears after the samples are calcined at 500 °C, and a new peak appears at $2\theta = 5.7^\circ$. The latter becomes very intense for the AT/50/8/500 sample, while rather weak for other samples. In addition, peaks corresponding to the anatase

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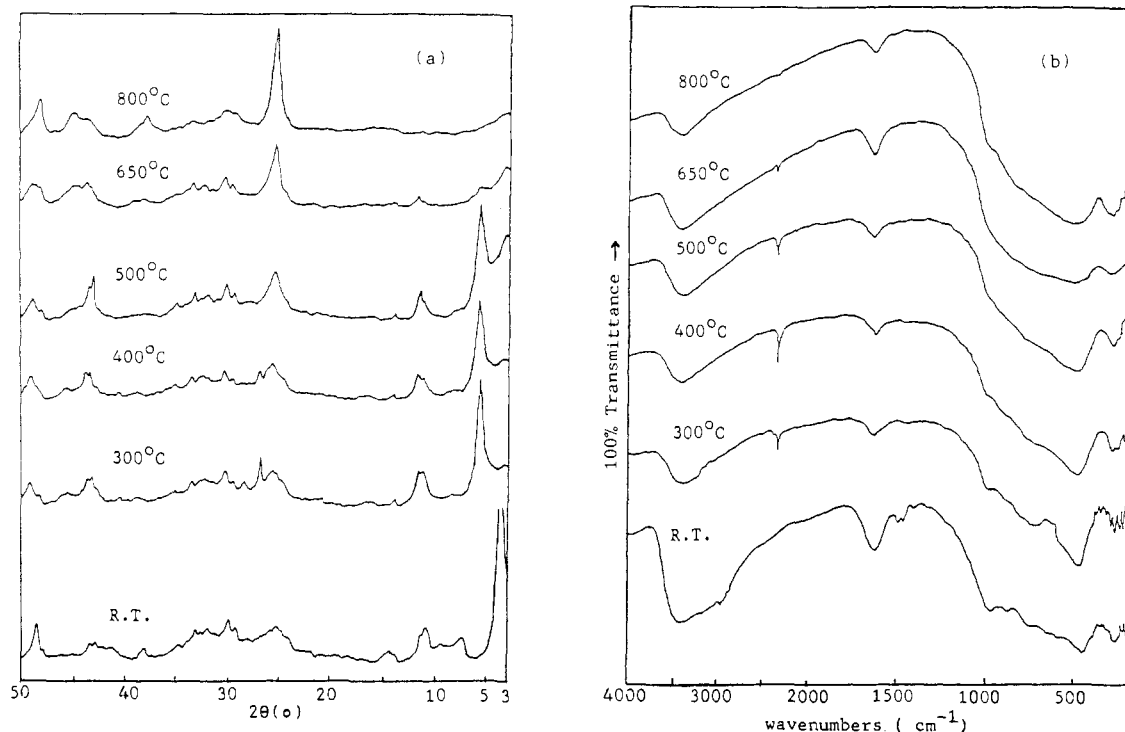


Figure 9. (a) XRD patterns and (b) IR spectra of sample AT/58/8 after heating at different temperatures.

phase ($2\theta = 25.3, 37.8, 48.0^\circ$) are also found in the XRD patterns of the calcined samples, but they are weaker and broader than those observed for samples prepared at room temperature. The amount of Al_{13}^{7+} Keggin ions accommodated between the titanate layers was analyzed with atomic absorption spectroscopy (Table I). The data indicate that about 90% of the exchange sites on the titanate are occupied by the Keggin ions at elevated exchange temperatures. However, unreasonably high Al content was found for the AT/100/6/500 sample, presumably due to the deposition of colloidal aluminum hydroxide formed at the high exchange temperature (100°C). The optimal exchange temperature, therefore, is in the range $50\text{--}70^\circ\text{C}$.

The thermal stability of Al_{13}^{7+} -exchanged tetratitanate was examined by thermogravimetric, XRD, and IR analyses. Those samples prepared at elevated exchange temperatures show similar weight loss curves (Figure 8). A weight loss with steep curvature occurs before 430°C ; then weight loss with smooth curvature extends up to 800°C . The former is assumed to be due to three processes in sequence: desorption of hydrating water molecules, decomposition of hexylammonium ions, and condensation of interlayer hydroxyl groups. In comparison with that of hexylammonium tetratitanate complex, these processes occur at relatively higher temperatures. Blocking by interlayer Al_{13}^{7+} Keggin ions is considered to account for the shifting. XRD analysis shows that the interlayer distance held by hexylammonium ions at 21.6 \AA decreases to 15.3 \AA after the sample is heated at 300°C (Figure 9a). The correlated IR spectra reveal that hexylammonium ions are decomposed at this temperature because peaks around 1450 and 2900 cm^{-1} corresponding to N-H and C-H vibration are missing (Figure 9b). Moreover, CO_2 is formed and contributes to the peak at 2340 cm^{-1} . The relief of trapped CO_2 molecules is likely the explanation for the gradual weight loss observed at high temperatures on the TGA curves. The interlayer spacing of 15.3 \AA collapses after the pillared sample is heated at 650°C . After the sample is heated at 800°C , the most crystalline phase observed is anatase TiO_2 .

Table II shows the increase in surface areas of the calcined samples of Al_{13}^{7+} -pillared tetratitanate complexes over that of the starting material, $\text{K}_2\text{Ti}_4\text{O}_9$. The surface areas of the former ranged from 120 to $250\text{ m}^2/\text{g}$. Since zeolitic structures usually have surface areas in the range of $300\text{ m}^2/\text{g}$ or higher, the interlayer space of the pillared titanates is considered to contribute very little to the surface areas. The porosity of these calcined samples is

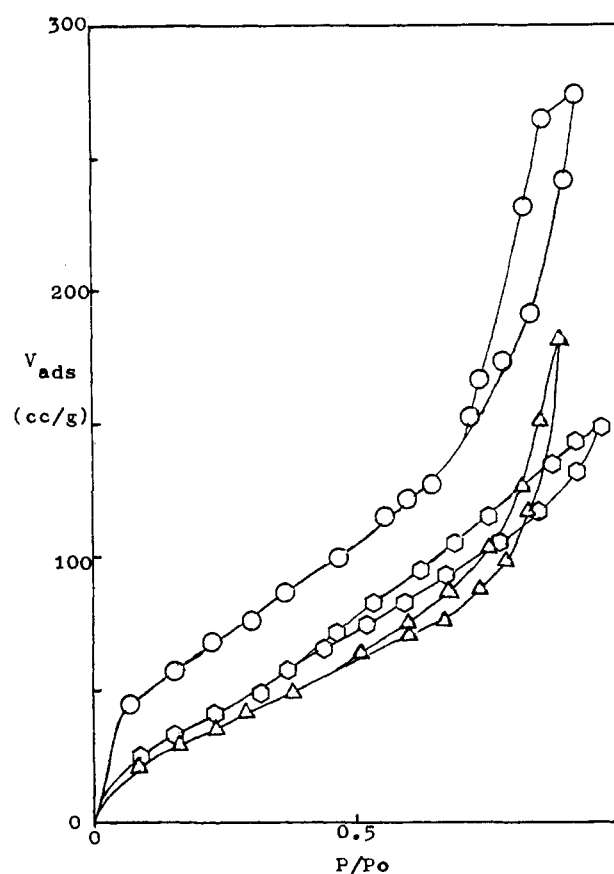


Figure 10. Nitrogen adsorption-desorption isotherms of Al_{13}^{7+} -pillared tetratitanate: \circ , AT/100/6; Δ , AT/50/8; \square , AT/25/120.

examined in terms of N_2 adsorption-desorption isotherms and is illustrated in Figure 10. The hysteresis of the curves demonstrates that these compounds are porous; however, the average diameters of the pores, estimated on the basis of the Kelvin equation,²⁴ are

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Table II. Surface Areas of Calcinated Al_{13}^{7+} -Tetratitanate Samples

sample	surf area, m^2/g	sample	surf area, m^2/g
AT/25/120/500	139	AT/100/1/500	176
AT/50/8/500	148	AT/100/6/500	254
AT/60/4/500	153	$\text{K}_2\text{Ti}_4\text{O}_9^a$	58
AT/70/7/500	122		

^aStarting material.

in the range of 10 nm. The diameter of Al_{13}^{7+} Keggin ions is ca. 9 Å, which will be the pore diameter if zeolitic pores are formed between the layers. Therefore, the observed porous structures are presumably due to defects in the structure and to void space at the boundary of different phases, considering that the crystallinity is rather poor and anatase TiO_2 forms upon calcination. Pinnavaia et al.²⁵ have reported that the porous structures of pillared clays are dependent upon the drying processes. This topic will be further investigated and reported in a separate paper dealing with the catalytic properties of the Al_{13}^{7+} -pillared tetratitanate.

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Conclusion

Our results demonstrate that layered tetratitanate compounds can be pillared with Al_{13}^{7+} Keggin ions. The resultant complex has an interlayer distance of 15.3 Å. Methods applied were not similar to those used to pillar clays. Because tetratitanates do not swell in water, the interlayer spacing has to be propped open by alkylammonium ions. The open layers then facilitate the replacement of alkylammonium ions by Al_{13}^{7+} Keggin ions. In order to avoid other cations in the solution competing for ion-exchange sites, alkylamines are used to hydrolyze AlCl_3 . The formation of Al_{13}^{7+} Keggin ions in the alkylamine-hydrolyzed AlCl_3 solutions was confirmed by ^{27}Al NMR spectra. Hexylammonium ions were found more stable in maintaining the interlayer distances of tetratitanates than butylammonium ions during the exchange process. The hexylammonium tetratitanate complex, when exchanged with hexylamine-hydrolyzed AlCl_3 solutions, leads to the formation of an Al_{13}^{7+} -pillared complex. These pillared compounds after calcination at 500 °C demonstrate medium-sized-pore structures and have fairly high surface areas.

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Isomerization of Binuclear Amidate-Bridged Platinum(II) Amine Complexes: A ^{195}Pt NMR Investigation

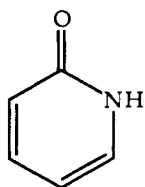
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^{195}Pt NMR spectroscopy has been used to identify and follow the reversible stereochemical rearrangement of the head-to-head (HH) isomer of $[\text{Pt}_2(\text{en})_2(\text{C}_5\text{H}_4\text{NO})_2](\text{NO}_3)_2$, where en = ethylenediamine and $\text{C}_5\text{H}_4\text{NO}^-$ is the α -pyridonate anion, to form the head-to-tail (HT) isomer in aqueous solution. Kinetic studies of the reaction established the rate law to be $-d(\text{HH})/dt = d(\text{HT})/dt = k_f[\text{HH}] - k_r[\text{HT}]$, an approach-to-equilibrium expression for which $K_{\text{eq}} = k_f/k_r$ and $k_{\text{obs}} = k_f + k_r$. For a typical run at 39 °C and pH 6.5 in 0.04 M phosphate buffer, $k_f = 7.4 (2) \times 10^{-5} \text{ s}^{-1}$, $k_r = 13.9 (2) \times 10^{-5} \text{ s}^{-1}$, and $K_{\text{eq}} = 0.53$. Temperature-dependent rate measurements revealed ΔH^\ddagger and ΔS^\ddagger to be 114 (5) kJ mol⁻¹ and 40 (10) J mol⁻¹ K⁻¹, respectively, values characteristic of a dissociative rate-determining step in the reaction mechanism. The suggestion that the isomerization is dissociatively activated is supported by the failure of DMSO to accelerate the rate, as would be expected for an associative mechanism, and the fact that the *cis*-diammineplatinum(II) analogue isomerizes at least 70 times slower than the sterically hindered ethylenediamine complex. The latter result is ascribed to steric strain in the $[\text{Pt}_2(\text{en})_2(\text{C}_5\text{H}_4\text{NO})_2]^{2+}$ complex, a consequence of nonbonded interactions between the hydrocarbon chains of the ethylenediamine ligands in two adjacent coordination planes. The isomerization reaction was shown to be intramolecular by the failure of added 6-methyl- α -pyridone or $[\text{Pt}(\text{en})(\text{H}_2\text{O})_2]^{2+}$ to affect the rate of product distribution. A mechanism is presented in which Pt-N(α -pyridonate) bond breaking is postulated to occur in the HH \rightarrow HT rearrangement process.

Introduction

Binuclear complexes bridged by two ligands are known to form in the reaction of the anticancer drug *cis*-diammineplatinum(II) (*cis*-DDP) with various amidate ligands including α -pyridone,^{1,2}



α -pyridone, $\text{C}_5\text{H}_4\text{NHO}$

a pyrimidine analogue, 1-methylcytosine,³ 1-methylthymine,^{4,5} 1-methyluracil,^{6,7} 1-methylhydantoin,⁸ 2-mercaptopyridine,⁹ and α -pyrrolidone.¹⁰ This chemistry was initially discovered in attempts to understand the interactions of the platinum(II) complexes with constituents of the proposed target of *cis*-DDP, DNA. The reactions gave rise to intensely colored blue compounds, which

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