

are continuing our anomalous scattering synchrotron experiments at the Pb edge, to investigate the possibility of a substitutional modulation related to the displacement waves described in this report.

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Interactions of Water-Soluble Porphyrins and Metalloporphyrins with Smectite Clay Surfaces

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Two simple water-soluble meso-substituted porphyrins were ion-exchanged into the interlayer space of montmorillonite, hectorite, and fluorhectorite. The porphyrins studied were the chloride salts of tetrakis(1-methyl-4-pyridiniumyl)porphyrin (TMPyP) and tetrakis(*N,N,N*-trimethyl-4-aniliniumyl)porphyrin (TAP) and the corresponding metalloporphyrins $\text{Fe}^{\text{III}}\text{TAP}$, $\text{Fe}^{\text{III}}\text{TMPyP}$, and $\text{Co}^{\text{II}}\text{TMPyP}$. These were ion-exchanged into H-, Li-, Na-, Ca-, Cu-, Co-, VO-, and Fe-montmorillonites and fluorhectorites. The porphyrins are diprotonated in H- and transition-metal-ion-exchanged clays. In group IA and IIA exchanged clays the porphyrins are mainly diprotonated but also exist as free bases. TAP is partially metallated in Cu-montmorillonite. Metalloporphyrin is released into solution after free bases react with Cu- and Co-clays. When metalloporphyrins are ion-exchanged into Ca-montmorillonite and Li-fluorhectorite, stable metalloporphyrin-clay complexes form. TAP and metallo-TAP porphyrins often display larger than expected basal spacings in X-ray diffraction (XRD) spectra that are possibly due to orientation effects. Irreversible changes occur in XRD and UV-visible absorption spectra after heating the porphyrin-clay complexes at only 160 °C.

Introduction

The class of crystalline aluminosilicates with controlled microstructures include zeolites, with pores and channels, and clays, which have two-dimensional layered structures. Within the past few years considerable research has been directed at new uses of such aluminosilicates as advanced materials.¹ Potential applications are based on the ability of these unique structures to selectively incorporate and exchange species within the void spaces on a molecular scale. The conductive properties of zeolites and clays can be altered to allow their use as solid electrolytes, as membranes in ion-selective electrodes, and as host structures for cathode materials in battery systems.¹ Electrode surfaces modified with clays² and pillared clays³ offer both high chemical stability and known and potentially controllable structural features. Studies utilizing zeolite-modified electrodes that interact with water-soluble porphyrins involve photochemical hydrogen evolution,⁴ current rectification and electron trapping,⁵ and electroassisted catalytic oxidation.⁶ However, porphyrin molecules are too large to fit inside the pores and channels of zeolites. Incorporation of porphyrins into the much larger interlayer regions of clays is possible and, in addition, also provides the opportunity of orientation control. The elucidation of the structural organization and photophysical properties of porphyrins in ordered molecular assemblies is a topic of current interest for their use as photoconductors, optical actuators, and chemical sensors.⁷

Smectite clay minerals possess a layered structure where negatively charged silicate layers are separated by positively charged cations and water molecules. The layer

charge of such smectites as montmorillonite and fluorhectorite arises mainly from isomorphous substitutions within the middle sheet of the 9.6-Å-thick clay layers. When the charge is compensated for by large inorganic and organic cations in the interlamellar space, the clay sheets are sufficiently separated^{8,9} to permit a wide variety of traditional adsorptive and catalytic uses.^{10,11} Porphyrins are well-known for both their biological and catalytic properties, and in each case their adsorption by the swelling, layer-lattice silicates is of interest.

This work was undertaken to examine the fundamental interactions of smectite clay surfaces with two cationic, water-soluble porphyrins and their metallo derivatives: the chloride salts of tetrakis(1-methyl-4-pyridiniumyl)porphyrin (TMPyP) and tetrakis(*N,N,N*-trimethyl-4-aniliniumyl)porphyrin (TAP). Figure 1 shows their structures. The literature to date concerning porphyrin-clay interactions can be divided into two general groups:

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Table I. Microanalysis Data and Calculated CEC Values for Porphyrin-Clay Complexes^a

complex	C, %	N, %	C/N		CEC, mequiv/100 g		
			exptl	theoret	free base	monocation	dication
Ca ²⁺ -mm	<0.3	<0.3					
TAP-mm	9.3	1.6	6.8	7.0	56	70	84
TMPyP-mm	7.5	1.5	5.8	5.5	55	69	83
TAP-1fh	7.8	1.3	7.0	7.0	47	59	71
TMPyP-1fh	8.3	1.7	5.7	5.5	62	78	93

^a mm = montmorillonite, bentolite L (reported CEC 80 mequiv/100 g). 1fh = synthetic Li⁺-fluorhectorite (reported CEC 90 mequiv/100 g). TAP = tetrakis(*N,N,N*-trimethyl-4-aniliniumyl)porphyrin. TMPyP = tetrakis(1-methyl-4-pyridiniumyl)porphyrin.

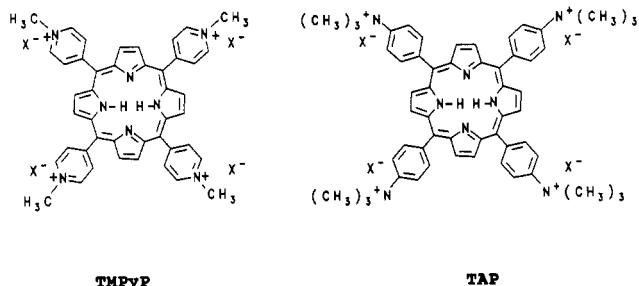


Figure 1. Water-soluble meso-substituted porphyrins tetrakis(1-methyl-4-pyridiniumyl)porphyrin (TMPyP) and tetrakis(*N,N,N*-trimethyl-4-aniliniumyl)porphyrin (TAP); X = chloride.

(1) those that probe geologically important interactions with naturally occurring biological macrocycles; (2) those that examine synthetic meso-substituted porphyrins of potential catalytic use. The first group of studies examines adsorption of alkylporphyrins on clays in aqueous media. The cationic form of hemin¹² was reported to ion-exchange into montmorillonite, with a subsequent increase in its thermal stability. Chlorophyllin is anionic, however, and was found to sorb only onto external edge surfaces of montmorillonite.¹³ Hematin, protoporphyrin, and hematoporphyrin,¹⁴ whether anionic or cationic dependent upon solution pH, were also found to sorb to such a low extent that no expansion of basal *d* spacing was detected. In general, the problems of low stability and purity and high structural complexity of natural porphyrins become limiting factors in such investigations. The second group of porphyrin-clay investigations consists mainly of those utilizing *meso*-tetraphenylporphyrin (TPP) and *meso*-tetrapyridylporphyrin (TPyP) and their metallo derivatives.¹⁵⁻¹⁸ It has been suggested¹⁵ that porphyrin hydrophilicity may be a significant factor in the stability of metalloporphyrins on clays.

Since protonation occurs on the pyrrolic nitrogens of porphyrins, the following species need to be considered while examining their interactions with acidic clay surfaces: the free bases TAP and TMPyP (or H₂TAP and H₂TMPyP), the monocations (H₃TAP⁺ and H₃TMPyP⁺), and the dications (H₄TAP²⁺ and H₄TMPyP²⁺). For TAP, pK₃ (free base → monocation) occurs at 4.11 and pK₄ at 3.95 (monocation → dication).¹⁹ H₄TMPyP²⁺ forms at pH 4.²⁰ Brønsted acidity of smectites, which depends

upon the type of exchangeable cation and the amount of water present, falls in a pK_a range of approximately 1–5.²¹ This easily overlaps the protonation range of porphyrins, and such equilibria and therefore expected to take place.

Experimental Section

Materials. Bentolite L, a Ca²⁺-montmorillonite supplied by E.C.C. America Inc., a Southern Clay Products subsidiary, TX, was chosen since it has been treated to remove all but 0.2 wt % iron. The cation-exchange capacity (CEC) is 80 mequiv/100 g, as stated by the supplier. The general formula²² for a montmorillonite is M⁺_x[(Al_{4-x}Mg_x)Si₄O₂₀(OH)₄]. SWy-1, a Wyoming Na⁺ montmorillonite, and STx-1, a Texas Ca²⁺-montmorillonite, were obtained from the Source Clay Repository. Hectabrite AW, a purified natural hectorite, was supplied by the American Colloid Co., Illinois. Li⁺-fluorhectorite, Li_{0.7}[(Mg_{5.3}Li_{0.7})Si₄O₂₀(F)₄], was synthesized by a sintering reaction at 800 °C according to Barrer and Jones,²³ who report a CEC value of 90 mequiv/100 g for this preparation. All transition-metal salts were reagent grade chloride salts, except for reagent grade LiNO₃ and VOSO₄·H₂O, and used as 0.1 M aqueous solutions for ion exchange of the clays. H⁺-montmorillonite was prepared by ion-exchange of bentolite L with NH₄Cl followed by heating at 250 °C for 2.5 days (*d*₀₀₁ = 12.4 Å). Centrifugation was used to isolate and wash all ion-exchanged products, which were then air-dried. VO²⁺ clays were made fresh and kept wet to prevent oxidation (clay color changes from blue to green). The water used was both distilled and deionized.

All porphyrins were purchased from Midcentury Co., Posen, IL, as chloride salts and used without further purification. Thermal gravimetric analysis revealed 11.5 wt % H₂O (from 25 to 180 °C) for tetrakis(1-methyl-4-pyridiniumyl)porphyrin (TMPyP^{Cl}) [C₄₄H₃₈N₈Cl₄·6H₂O (MW = 928)] and 16.4 wt % H₂O (from 25 to 140 °C) for tetrakis(*N,N,N,N*-trimethyl-4-aniliniumyl)porphyrin (TAP^{Cl}) [C₅₆H₆₀N₈Cl₄·11H₂O (MW = 1186)]. Similarly for the metalloporphyrins, Fe^{III}TMPyP^{Cl}, Fe^{III}[C₄₄H₃₈N₈Cl₅·7H₂O], MW = 1035; Co^{II}TMPyP^{Cl}, Co^{II}[C₄₄H₃₈N₈Cl₄·7H₂O], MW = 1003; and Fe^{III}TAP^{Cl}, Fe^{III}[C₅₆H₆₀N₈Cl₄·9H₂O], MW = 1239. Ion-exchange of porphyrin salts into clays was performed by slurring 0.25 g of clay in 50 mL of 1 × 10⁻³ M aqueous solutions for 24 h.

Characterization. X-ray powder diffraction was done on a Scintag PAD-V instrument using Cu K α radiation and a hyperpure germanium solid-state detector; scan rates varied from 0.5 to 1° 2θ/min. Samples were usually run as oriented films on horizontally held glass slides, made by mixing clay and water to a paste in a mortar with subsequent air-drying on the slide. Heterites preferentially oriented to a marked degree. Data were collected on a DG Desktop computer system.

UV-visible spectroscopy of solutions was performed on a Shimadzu UV-160 instrument in the slow analysis mode. Diffuse reflectance absorption spectra were recorded on a Cary 2390 spectrometer equipped with an integrating sphere accessory. All spectra were scanned at 1 nm/s; appropriate reference samples were run as automatic base lines prior to sample runs. The same slides used for XRD analysis were mounted vertically over the open port (about 1-cm diameter). Thermal gravimetric analysis (TGA) was done using a Cahn 121 microbalance interfaced to an

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Table II. d (001) Spacings (Å) in Free Base Porphyrin Complexes with Various Ion-Exchanged Clays

ion-exchanged clay	TMPyP ^d	TAP ^e
H ⁺ -montmorillonite	13.5	14.3
Li ⁺ -montmorillonite	15.7	18.3
Na ⁺ -montmorillonite ^a	14.3	15.9
Ca ²⁺ -montmorillonite	14.9	15.7
Ca ²⁺ -montmorillonite ^b	15.0	15.2
Cu ²⁺ -montmorillonite	14.3	18.0, 15.2
Co ²⁺ -montmorillonite	15.2	nd ^f
VO ²⁺ -montmorillonite	14.3	16.2
Fe ³⁺ -montmorillonite	13.9	14.7
Li ⁺ -fluorhectorite	14.0	17.7, 14.5
Ca ²⁺ -hectorite ^c	nd	15.7
Cu ²⁺ -fluorhectorite	14.1	18.0, 15.2
Co ²⁺ -fluorhectorite	14.1	nd
VO ²⁺ -fluorhectorite	13.9	15.2
Fe ³⁺ -fluorhectorite	13.9	15.0

^aSWy-1. ^bSTx-1. ^cHectabrite AW. ^dTMPyP = tetrakis(1-methyl-4-pyridiniumyl)porphyrin. ^eTAP = tetrakis(*N,N,N*-trimethyl-4-aniliniumyl)porphyrin. ^fnd = not determined.

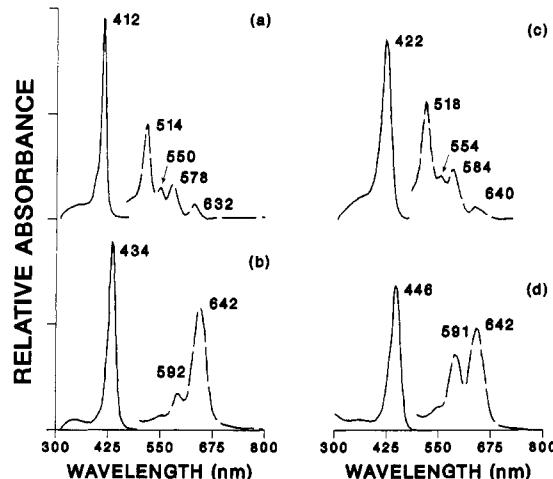


Figure 2. Solution UV-visible absorption spectra of tetrakis(*N,N,N*-trimethyl-4-aniliniumyl)porphyrin (a) as the free base in water and (b) as the dication in 1 N HCl, and tetrakis(1-methyl-4-pyridiniumyl) porphyrin (c) as the free base in water and (d) the dication in 1 N HCl. Dashed curves represent more concentrated solutions.

IBM PC for data collection and analysis. Samples were run under nitrogen at 10 °C/min.

Results

Microanalysis and CEC Measurements. The interlayer cations of clays are mobile and can be exchanged to various degrees by other ions. Resulting cation-exchange capacity (CEC) measurements of certain ions therefore reflect the degree to which a clay has been exchanged. The percent of carbon and nitrogen present in porphyrin-exchanged clays was determined by microanalysis, and CEC values were calculated from this data. Table I lists three CEC values for each of the three possible protonated forms of the porphyrins: the free base has a charge of +4 (H_2P), the monocation a charge of +5 (H_3P^+), and the dication a charge of +6 (H_4P^{2+}). Comparison of the theoretical vs experimental C/N ratios indicate the porphyrins are incorporated intact and have not degraded.

X-ray Diffraction. The d spacing (001 reflection along the c axis), or d (001), measures the distance between basal layers of the clay and typically varies between 10 and 20 Å depending upon the size of the exchangeable cation present. Table II lists the d (001) values for several different homoionic clays when ion-exchanged with free base porphyrins.

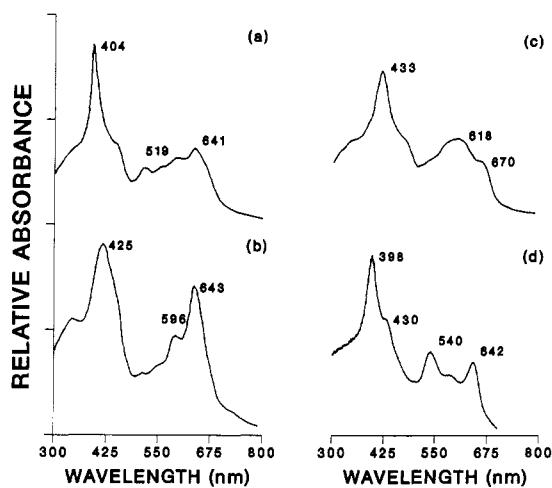


Figure 3. Diffuse reflectance absorption spectra of tetrakis(*N,N,N*-trimethyl-4-aniliniumyl)porphyrin (TAP) in (a) Ca-montmorillonite and (b) H-montmorillonite, (c) tetrakis(1-methyl-4-pyridiniumyl)porphyrin in Fe-montmorillonite, and (d) TAP in Cu^{2+} -fluorhectorite.

Table III. Diffuse Reflectance Absorption Data of Porphyrin Complexes with Ion-Exchanged Clays^a

clay	wavelength, nm	assgn
		TAP
Ca ²⁺ -mm	404, 519, 600, 641	TAP, H_4TAP^{2+}
H ⁺ -mm	425, 596, 643	H_4TAP^{2+}
Ca ²⁺ -mm ^b	418, 595, 640	H_4TAP^{2+}
Na ⁺ -mm ^c	400, 454, 523, 565, 604, 656	not assigned
Li ⁺ -hect	410, 450 sh, 520, 595, 640	TAP, H_4TAP^{2+}
		TMPyP
Ca ²⁺ -mm	423, 600	TMPyP, H_4TMPyP^{2+}
H ⁺ -mm	438, 615	H_4TMPyP^{2+}
Li ⁺ -hect	431, 609	TMPyP, H_4TMPyP^{2+}

^amm = montmorillonite; hect = fluorhectorite; sh = shoulder; TAP = tetrakis(*N,N,N*-trimethyl-4-aniliniumyl)porphyrin; TMPyP = tetrakis(1-methyl-4-pyridiniumyl)porphyrin. ^bSTx-1. ^cSWy-1.

UV-Visible Absorption Spectra of Porphyrins. Absorption bands in the UV-visible region occur in two sets for porphyrins. The Soret band is characterized by a large extinction coefficient and lies in the 400–450-nm range. A second set of weaker bands (Q bands) occurs between 450 and 700 nm. Free bases have four weak Q bands; protonation to the dication decreases this number to two and also causes the Soret band to shift to higher wavelength. This behavior is highlighted in Figure 2 for both TAP and TMPyP in aqueous solutions. UV-visible absorption spectra of the free base porphyrins (H_2P) in aqueous solution are displayed along with their protonated dication (H_4P^{2+}) forms in 1 N HCl. The solutions change color from maroon to green upon protonation. The characteristics of these solution spectra were used to assign the species present in the various clays.

Free Base Porphyrin-Clay Complexes. The porphyrins were exchanged into Li⁺-fluorhectorite, Ca²⁺-, H⁺-, and Fe³⁺-montmorillonites, and natural, unprocessed, Ca²⁺- and Na⁺-montmorillonites (STx-1 and SWy-1, respectively). Selected diffuse reflectance (DR) spectra are shown in Figure 3. Figure 3a–c is representative of free base vs dication porphyrin intercalation. Table III summarizes DR data for the other clay systems examined. Examination of decants after ion-exchange showed that excess porphyrin left in solution always occurred as the free base form. Molecular modeling of the different protonated forms of TAP revealed that substantially different geometries occur between the free base and the dication;

Table IV. UV-Visible Absorption Data of Decants from Porphyrin Complexes with Transition-Metal-Ion-Exchanged Montmorillonites^a

ion in clay	color	wavelength, nm	assgn
TAP			
Fe(III)	green	412, 514, 550, 580, 640	TAP, H ₄ TAP ²⁺
Cu(II)	rose	412, 430, 540, 643	Cu ^{II} TAP, H ₄ TAP ²⁺
TMPyP			
Fe(III)	maroon	422, 518, 554, 584, 640	TMPyP
Cu(II)	rose	424, 548	Cu ^{II} TMPyP
Co(II)	orange	432, 548	Co ^{II} TMPyP

^aTAP = tetrakis(*N,N,N*-trimethyl-4-aniliniumyl)porphyrin; TMPyP = tetrakis(1-methyl-4-pyridiniumyl)porphyrin.

Table V. Diffuse Reflectance Absorption Data of Porphyrin Complexes with Transition-Metal-Ion-Exchanged Montmorillonites^a

ion in clay	color	wavelength, nm	assgn
TAP			
Fe(III)	green	430, 594, 634	H ₄ TAP ²⁺
Cu(II)	dark green	403, 545, 590, 643	H ₄ TAP ²⁺ , Cu ^{II} TAP
TMPyP			
Fe(III)	green	433, 618, 670	H ₄ TMPyP ²⁺
Cu(II)	green	431, 592	H ₄ TMPyP ²⁺
Co(II)	green	422, 591	H ₄ TMPyP ²⁺

^aTAP = tetrakis(*N,N,N*-trimethyl-4-aniliniumyl)porphyrin; TMPyP = tetrakis(1-methyl-4-pyridiniumyl)porphyrin.

the molecular geometries for each are displayed in Figure 4.

Transition-Metal-Exchanged Clays. When combined, transition-metal-exchanged clays [Fe(III)-clays are orange, Cu(II)-clays are light blue, etc.] and maroon porphyrin solutions usually created a bright green slurry. UV-visible absorption data of decants are tabulated in Table IV for montmorillonites. All decants from fluorhectorite-exchanged clays showed similar behavior, with one exception: TAP-exchanged Cu(II)-fluorhectorite resulted in a brown solution with absorbances only at 412 and 539 nm. This result is characteristic of Cu^{II}TAP dissolved in water, which has absorbances at 411 and 538 nm only. Diffuse reflectance absorbance data for all porphyrin-montmorillonite samples are tabulated in Table V, and again most fluorhectorites behaved in a similar fashion. TAP exchanged into Cu(II)-fluorhectorite is displayed in Figure 3d. Assignments given in the tables were made in a fairly straightforward fashion by comparison with results of the free base porphyrin interactions with clays.

Metalloporphyrin-Clay Complexes. The classic UV-visible absorption spectrum of metalloporphyrins contains a Soret band slightly red-shifted from the free base and one or two Q bands between 500 and 650 nm. Figure 5 shows UV-visible absorption spectra for Fe^{III}TAP, Fe^{III}TMPyP, and Co^{II}TMPyP in solution and their diffuse reflectance absorption spectra after exchange with Ca²⁺-montmorillonite. Table VI lists the characteristics and assignments of metalloporphyrin-exchanged montmorillonite and Li⁺-fluorhectorite.

Thermal Stability. Changes in X-ray diffraction and diffuse reflectance absorbance behavior were noticeable after heating the porphyrin-clay complexes in air at only 160 °C for 2 days. The same glass slides used to collect data at room temperature were heated and then rewetted to probe whether the changes were reversible with water. Tables VII and VIII list XRD results of these experiments with montmorillonite and fluorhectorite complexes, respectively. Figure 6 shows DR spectra after heating the

Table VI. Characteristics of Metalloporphyrin-Exchanged Clay Complexes

complex	color	d(001), Å	assgn ^a
FeTAP-montmorillonite	brown	18.0	Fe ^{III} TAP
FeTMPyP-montmorillonite	olive-green	16.7	Fe ^{III} TMPyP
CoTMPyP-montmorillonite	brown	14.5	Co ^{II} TMPyP
FeTAP-fluorhectorite	brown	19.5, 15.9	Fe ^{III} TAP
FeTMPyP-fluorhectorite	olive-green	16.7	Fe ^{III} TMPyP
CoTMPyP-fluorhectorite	brown	14.7	Co ^{II} TMPyP

^aSpecies assigned to be present in clay.

Table VII. d Spacings of Porphyrin-Exchanged Montmorillonites^a upon Heating and Reexposure to Water

complex	d(001), Å		
	25 °C	160 °C	rewet
TAP-montmorillonite	15.7	15.0	15.2
TMPyP-montmorillonite	14.5	13.9	13.9
FeTMPyP-montmorillonite	16.7	16.7	16.7

^aClay used was bentolite L, a Ca²⁺-montmorillonite; TAP = tetrakis(*N,N,N*-trimethyl-4-aniliniumyl)porphyrin; TMPyP = tetrakis(1-methyl-4-pyridiniumyl)porphyrin.

Table VIII. X-ray Diffraction Data as a Function of Temperature for Free Base Porphyrin-Fluorhectorite Complexes^a

porphyrin	d(001), Å					
	25 °C	120 °C	160 °C	rewet	200 °C	270 °C
TAP	17.7, 14.5	15.0	14.7	14.7	14.5	13.3
TMPyP	14.0 br	13.9 sh	13.7	13.7	13.7	13.5

^abr = broad; sh = sharp; TAP = tetrakis(*N,N,N*-trimethyl-4-aniliniumyl)porphyrin; TMPyP = tetrakis(1-methyl-4-pyridiniumyl)porphyrin.

porphyrin-clay complexes. Rewetting was done by placing the slides in a vessel at 100% relative humidity for 3 days, or by exposure to distilled water mist for an atomizer. Neither treatment changed diffuse reflectance absorbance spectra noticeably. The changes in the d(001) region of X-ray diffraction spectra for TAP-fluorhectorite are shown in Figure 7 as a function of the amount of water present.

Discussion

Free Base Porphyrin-Clays. The diffuse reflectance spectra of porphyrin-exchanged montmorillonite clays are not identical with any of the solution spectra in Figure 2 for a combination of two reasons: (1) a mixture of species can occur and (2) there are solvent and matrix effects arising from the clay interlayer environment. The intensity of the Soret band decreases considerably upon complexation with clays¹⁵ and is always much smaller for the dication than for either the free base or metalloporphyrin. As a result, only a few percent of free base (or metalloporphyrin) will keep the Soret maximum at a low wavelength. Solvent effects can be responsible for Soret band wavelength shifts, such as the blue shift observed for Sn^{IV}TMPyP upon clay intercalation (424 → 417 nm).¹⁶

With the above information, Figure 3a of TAP-montmorillonite (Ca²⁺-clay) can be interpreted as a mixture of dication and free base. The intense Soret peak at 404 nm is due to a small amount of free base that is blue-shifted due to matrix effects; the peak at 519 nm is also due to TAP. The shoulder on the high wavelength side of the Soret peak and the strong Q bands at 600 and 641 nm are attributed to the dication H₄TAP²⁺. The color of the clay complexes is deep green, which also indicates a large amount of dication. As an example from the CEC values calculated in Table I, this mixture is 86% dication and 14% free base for TAP-montmorillonite. The CEC for TAP-fluorhectorite is considerably lower than the others,

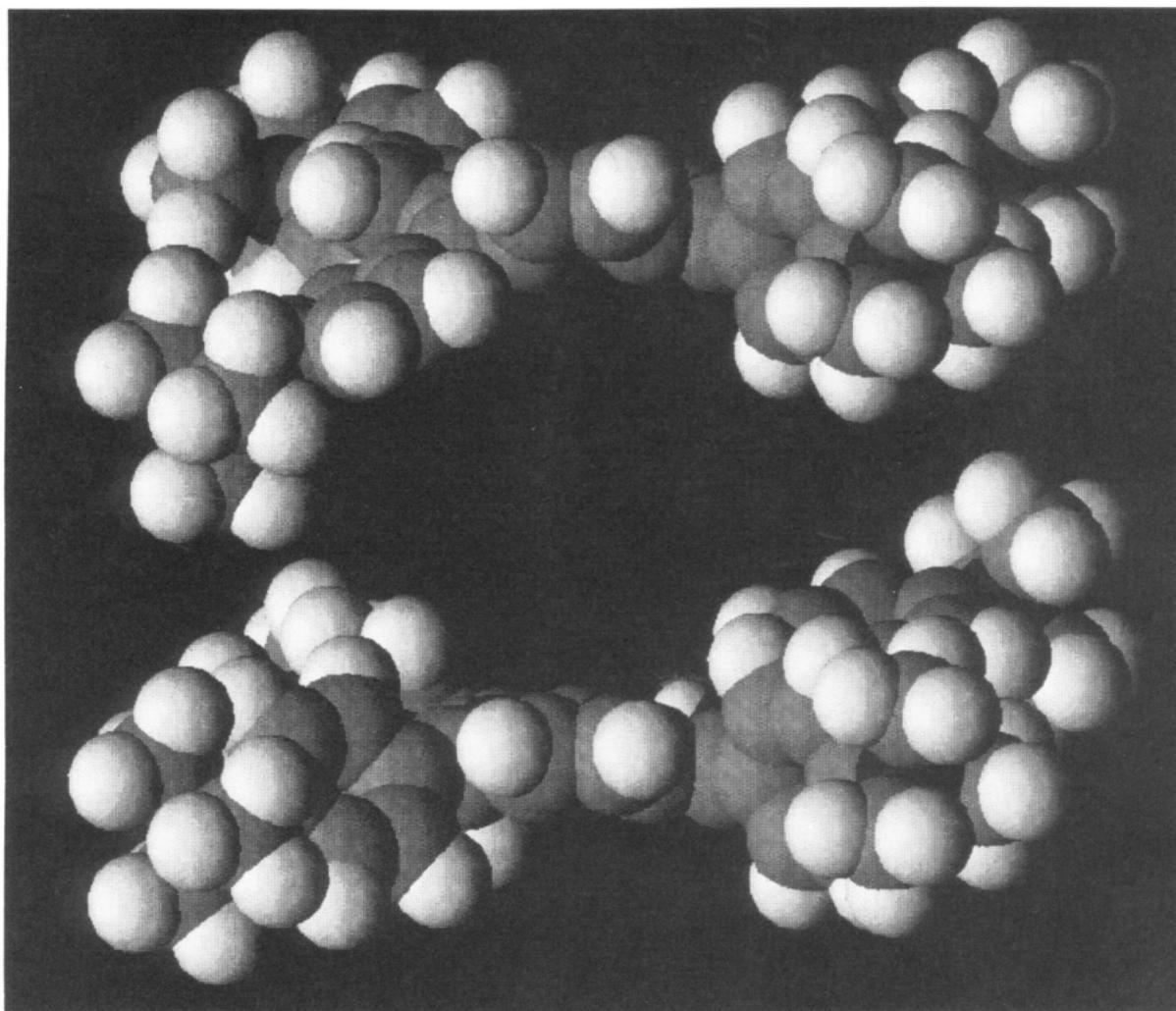


Figure 4. Space-filling molecular models of tetrakis(*N,N,N*-trimethyl-4-aniliniumyl)porphyrin as the free base (top) and the dication (bottom).

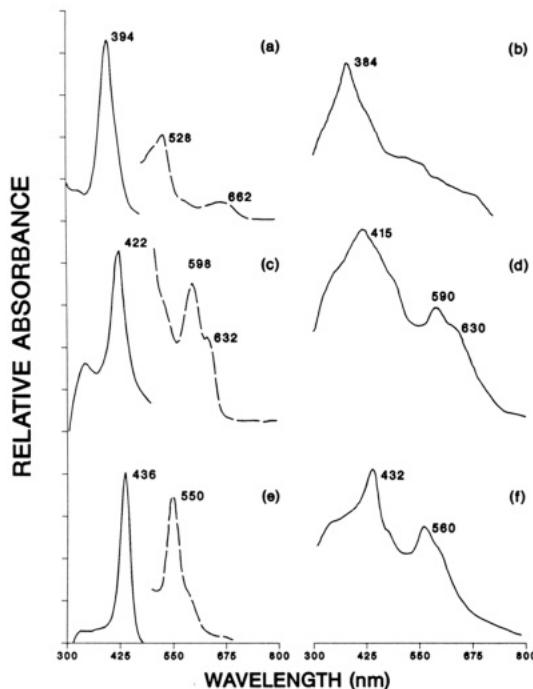


Figure 5. UV-visible absorption spectra of metalloporphyrins: Fe^{III}TAP in (a) 1 N HCl and (b) Ca-montmorillonite; Fe^{III}TMPyP in (c) water and (d) Ca-montmorillonite; Co^{II}TMPyP in (e) water and (f) Ca-montmorillonite. Dashed curves represent more concentrated solutions.

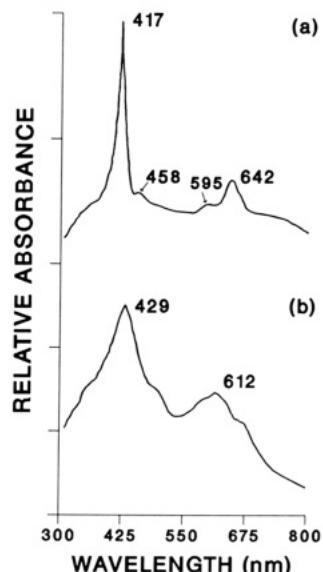


Figure 6. Diffuse reflectance absorption spectra of porphyrin-montmorillonite complexes after heating at 160 °C for 24 h: (a) tetrakis(*N,N,N*-trimethyl-4-aniliniumyl)porphyrin and (b) tetrakis(1-methyl-4-pyridiniumyl)porphyrin.

indicating that this clay is not fully exchanged with porphyrin.

The diffuse reflectance spectra for TMPyP-exchanged clays (Figure 3c, Table III) are not as readily interpretable.

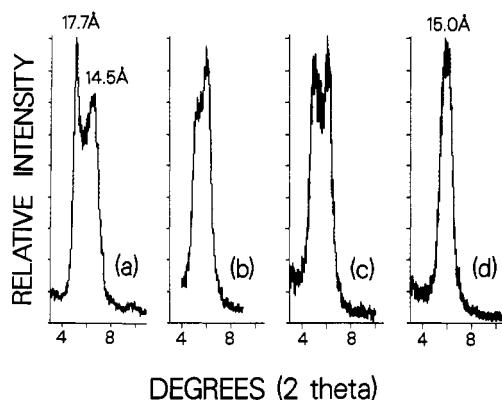


Figure 7. X-ray diffraction spectra of tetrakis(*N,N,N*-trimethyl-4-aniliniumyl)porphyrin-fluorhectorite complexes (a) as prepared, (b) after several weeks at ambient conditions, (c) reexposed to water, and (d) after heating at 120 °C for 24 h.

Baker et al.^{20a} demonstrated that the monocation H_3TMPyP^+ has a red-shifted Soret band and four Q-bands. Since TMPyP-clays display three poorly resolved Q bands, a monocation species is unlikely. Pasternack et al.²⁴ have shown that TMPyP does not dimerize or form aggregates in solution, so these types of species are also unlikely. Since the clay complexes are green, it can be inferred that the free base form, which is maroon, is a minor contributor. From the microanalysis information and CEC values in Table I, 63% dication and 37% free base would result if behavior was analogous to TAP-montmorillonite. In an attempt to definitively assign the TMPyP porphyrin species present, exchange of highly acidic H^+ -montmorillonite was examined to determine if an increase in the concentration of dication occurred. This was noticeably successful for TAP, where bands for free base disappeared and the Soret weakened and shifted to 425 nm (see Figure 3b). The Soret peak shifted significantly for TMPyP/H^+ -montmorillonite ($423 \rightarrow 438 \text{ nm}$), but the Q-band region did not change. When highly acidic Fe^{3+} -clays²⁵ are used, the complexes are the brightest green in color, indicative of dications, and the diffuse reflectance spectra match those of H^+ -exchanged clays (Figure 3c). TMPyP exchanged into Fe^{3+} -montmorillonite is therefore most likely present as the dication. Data for STx-1 exchanged clays are more like these acidic clays (Table III), even though the counterion is Ca^{2+} . This is attributed to the higher concentration of iron present in this natural, unprocessed, clay. Overall, acidity of the clays follows the polarizability of the exchangeable cations²⁶ quite well: $\text{Fe}^{3+} \gg \text{Cu}^{2+} \simeq \text{Co}^{2+} > \text{Ca}^{2+} \gg \text{Na}^+ \simeq \text{Li}^+$. TMPyP exchanged into Ca^{2+} -montmorillonite is therefore probably a mixture of dication and free base, as is the case for TAP, even though the Q-band region in the absorption spectrum never shows appreciable differences.

X-ray Diffraction. Stone and Fleischer²⁷ have demonstrated that for dications the substituents on the porphyrin nucleus are nearly coplanar with the macrocycle, while for free bases the substituents are significantly out of the plane. As a result, the observed thickness of an intercalated clay layer is expected to differ depending upon the type of porphyrin species present and its subsequent

molecular geometry. Molecular modeling of the different species possible for TAP is displayed in Figure 4. These models reveal that TAP is about $17 \times 17 \text{ \AA}^2$ in cross section, with a thickness of about 7.1 Å for the free base and 6.3 Å for the dication. Analogous behavior is expected for TMPyP, except that the thickness of this molecule is smaller due to less bulky substituents. As a result, when 100% dication is intercalated, it is expected that the $d(001)$ value should be about 1 Å less than when the free base is present in the clay interlayers. The d spacings are indeed a full angstrom less for both TAP and TMPyP exchanged into H^+ -montmorillonite (see Table II).

The interlayer spacing of porphyrin-exchanged clays is sometimes lower than expected when the clay layer (9.6 Å) is added to the dication porphyrin nucleus. Van Damme et al.¹⁷ also observed this phenomenon and suggested that tilting of meso substituents with respect to the tetrapyrrolic ring was more pronounced than in unrestricted compounds, leading to a more planar molecule. This also causes the large bathochromic shifts observed for the Soret bands due to increased resonance in the overall pyrrole ring. An interesting exception to the rather small d spacing occurs occasionally for exchanges involving TAP. Table II shows that Cu^{2+} -montmorillonite and Li^+ - and Cu^{2+} -fluorhectorite display two peaks in the $d(001)$ region of X-ray diffraction spectra. One of these, near 18 Å, is too large to be due to even the large free base porphyrin (9.6 Å clay layer + 7.1 Å free base = 16.7 Å) when not restricted at all. If the porphyrin macrocycle is not intercalated parallel to the clay layers but is instead tilted to some degree, then orientation effects are responsible. An estimated tilt angle can be calculated from the dimensions of TAP and the observed interlayer space. For instance, from molecular modeling the TAP dication is 17 Å long and 6.3 Å high. A basal spacing of 18.0 Å minus the clay layer (9.6 Å) leaves an interlayer space of 8.4 Å. In this case, the tilt angle is calculated to be about 7.2° and applies whether the porphyrin exists as the dication or is complexed by a metal ion (if the species is free base TAP then the estimated tilt angle is only 4.5°). Orientation can be examined by polarization methods using thin films of samples. Another possible explanation of the large d spacings may arise from dimerization of the porphyrin molecules. Since only monomers fluoresce, the possibility of dimerization can be probed by luminescence spectroscopy.²⁸

Transition-Metal-Ion-Exchanged Clays. Transition-metal-ion-exchanged clays reacted with free base porphyrins exhibit some interesting properties in addition to the acidity effects mentioned in the previous section. UV-visible absorption studies of the decants from porphyrin-clay exchanges show differences based on the specific transition-metal ion present in the interlayer space of the clay. For instance, when $\text{Fe}(\text{III})$ -clays are used, the species in solution after exchange are either the free base or the dication. When the exchangeable cations are $\text{Cu}(\text{II})$ or $\text{Co}(\text{II})$, however, absorption data indicate that the corresponding metalloporphyrins are formed and released into solution (Table IV). Diffuse reflectance absorption data of the porphyrin-clay complexes reveals that dications, not the metalloporphyrins, are retained on the clay surface. An exception is possible in the case of TAP exchanged into $\text{Cu}(\text{II})$ -clays. An absorption peak at about 540 nm in the DR spectrum (see Figure 3d) may be due to $\text{Cu}^{II}\text{TAPCl}$ dissolved in water absorbs at 411 and 538 nm only. Regardless of the transition-metal ion present

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in TMPyP-exchanged clays, the diffuse reflectance pattern always indicates dication (Table V, and all are similar to Figure 3c). Overall, results from experiments using transition-metal-ion-exchanged clays compare well with previous studies using tetraphenylporphyrin (TPP).^{17,18} The only difference from a study involving tetrapyridylporphyrin (TPyP) is that the Co^{II}TPyP formed was retained on the clay surface,¹⁷ whereas in this work only dication is held in the interlayers of Co(II)-clays.

Metalloporphyrin-Clay Complexes. Comparisons of solution spectra with diffuse reflectance absorption spectra of metalloporphyrin-exchanged clay complexes (see Figure 5) demonstrate that metalloporphyrin is held intact within the clay interlayers. Spectra of Fe^{III}- and Co^{II}TMPyP in aqueous solution match closely with those of the corresponding clay complexes. The exchanged montmorillonites are represented in Figure 5; exchanged fluorhectorites display nearly identical results. The absorption spectrum of Fe^{III}TAP dissolved in aqueous solution contains a Soret band at 406 nm and Q bands at 565 and 602 nm. Fe^{III}TAP dissolved in 1 N HCl (Figure 5a), however, shows a wholly different pattern. In addition, the color changes from yellow-green to orange. Fe(III) metalloporphyrins are in stability class II,²⁹ which means that they are completely demetalated only in 100% H₂SO₄. The modifications in the absorption spectrum are instead explained by the known sensitivity of the UV-visible spectrum to the associated anion of +3 cations. For example, the Q band at 508 nm for Fe^{III}TPPCl is red-shifted to 590 nm for Fe^{III}TPPOH.³⁰ It is the spectrum of Fe^{III}TAP dissolved in 1 N HCl that most closely correlates with the clay complex. The most probable axial ligands in the adsorbed state are water molecules or oxygen atoms from the clay lattice.¹⁵ Basal spacings (Table VI) are also similar for both montmorillonites and fluorhectorites. The exchanges involving TAP, in this case Fe^{III}TAP, again result in large basal spacings.

The decants from metalloporphyrin-clay exchanges are either clear or contain only metalloporphyrin species. This is for the most part consistent with the findings of Bergaya and Van Damme,¹⁵ who examined metallo-TPPs on clay surfaces. One difference involves Co^{II}TPP, which they reported was retained on the clay surface only as the dication. In this work Co^{II}TMPyP is quite stable on the surfaces of smectites. Van Damme et al.¹⁷ reported that Fe^{III}TPP completely demetalated and Fe^{III}TPyP partially demetalated on clay surfaces. In this study the Fe(III) porphyrins are also adsorbed intact in the clay mineral interlayers. Both Fe(III) and Co(II) metalloporphyrins are in stability class II and are therefore not expected to demetalate on smectite clay surfaces. Employing aqueous versus organic solvents may cause the enhanced stability of metalloporphyrins on clays that is observed in the present work.

Thermal Stability. Observable changes in X-ray diffraction and UV-visible absorption spectra are extremely slight until 160 °C. Figure 6 shows the diffuse reflectance spectra for exchanged montmorillonites, and fluorhectorites behaved in a similar manner. The changes for TMPyP-clays heated to 160 °C are subtle. For example, UV-visible absorption bands for TMPyP-montmorillonite are shifted from 423 to 429 nm and 605 to 612 nm, and the basal spacing decreases by 0.6 Å. TAP-clays display Soret peaks red-shifted from about 404 to 417 nm with

similar decreases in the *d* spacings (e.g., 0.7 Å for TAP-montmorillonite). The surface Brønsted acidity of clay surfaces is known to increase as the amount of water decreases, because coordinated water molecules are more easily dissociated by the polarizable exchangeable cations. Removal of interlayer water molecules from porphyrin-clay complexes should increase the acidity of the clay, which may then induce complete porphyrin dication formation in the clays containing a mixture of free base and dication. Reexposure of the clay complexes to water does not restore the original characteristics. Therefore, irreversible changes appear to occur at relatively low temperatures. Fe^{III}TMPyP-montmorillonite is not affected by mild heat treatments, which suggests that the metal ion has stabilized the porphyrin macrocycle toward these conditions. Further studies into the thermal behavior and stability of these complexes is currently underway.

Since the phenomenon of two *d* spacings displayed for TAP-fluorhectorite is of interest, the XRD spectra were monitored as a function of temperature and water content. The highest spacing at 17.7 Å decreases in intensity simply upon sitting for several weeks at ambient conditions (Figure 7b). It can, however, be restored if water is added back to the complex. After heating at only 120 °C, this peak disappears. Because the basal spacing appears to be related to the amount of water present, this further suggests that orientation effects are the predominant factor for the largest *d* spacing, rather than, for example, dimerization.

Conclusions

The ability of metalloporphyrins to penetrate into and remain bonded to the silicate layers of smectite clays encourages the use of such minerals as inorganic supports for bivalent metalloporphyrins, which are known to be catalysts for oxidative dehydrogenation³¹ and to act as reversible oxygen carriers. They could also serve as supports for model compounds of the monooxygenase enzyme cytochrome P-450, such as the Mn(III) and Fe(III) porphyrins that are currently being examined as homogeneous alkane activation catalysts.³² A preliminary investigation into the partial oxidation of methane using supported porphyrin has in fact been published.³³ In addition, the relatively new photochemical and electrochemical uses of the water-soluble porphyrins in zeolite systems could be extended to clay systems. The advantage of direct incorporation of porphyrin on the support may promote higher efficiencies. It is interesting that in some situations involving tetrakis(*N,N,N*-trimethyl-4-aniliniumyl)-porphyrin a certain percentage of the intercalated species is less "restricted" than others. The large *d* spacing observed in XRD spectra is probably due to molecules that are not as confined by the clay layers and are instead oriented at a small angle from parallel with the layers. This has implications for interactions between complexed metal ions, which is a prerequisite for practical applications of porphyrin assemblies.

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Registry No. TMPy-Cl, 92739-63-4; TAP-Cl, 92739-64-5; FeTMPyP-Cl, 126425-09-0; FeTAP-Cl, 126425-10-3; CoTAP-Cl, 126425-11-4; H, 12408-02-5; Na, 7440-23-5; Li, 7439-93-2; Cu, 7440-50-8; Co, 7440-48-4; VO, 20644-97-7; Fe, 7439-89-6; Ca, 7440-70-2.