material and 647 mg (17%) of I as shiny metallic copper-colored plates, decomposition above ~180 °C without melting. Anal. Calcd for $C_{12}H_{21}B_9Fe_2$: C, 38.51; H, 5.66; B, 26.00; Fe, 29.84. Found: C, 38.15; H, 5.50; B, 25.00; Fe, 28.61. High-resolution mass measurement calcd for $^{12}C_{12}{}^{1}H_{21}{}^{11}B_9{}^{56}Fe_2{}^+$ 376.1168, found 376.1202. Infrared spectrum (Nujol mull): 3070 (w), 2600 (w), 2510 (vs), 2470 (vs), 1420 (s), 1120 (w), 1130 (w), 1070 (m), 1060 (w) 1025 (s), 1010 (m), 965 (m), 935 (w), 925 (w), 910 (w), 905 (w), 885 (m), 875 (w), 860 (w), 850 (s), 835 (s), 755 (w), 738 (m), 728 (m), 720 (m) cm^{-1}.

A yellow-brown band was eluted from the column in 60% CH_2Cl_2/hexane which upon rotary evaporation of solvent produced 60 mg (1.6%) of green-brown crystals of III, $(C_5H_5Fe)_2C_2B_8H_9OH$, mp >300 °C. Mass measurement calcd for $^{12}C_{12}{}^{1}H_{20}{}^{11}B_8{}^{56}Fe_2{}^{16}O^+$ 380.0957, found 380.0973; calcd for $^{12}C_{11}{}^{13}C^{1}H_{20}{}^{11}B_8{}^{57}Fe_2{}^{16}O^+$ 383.1000, found 383.1003. Infrared spectrum (Nujol mull): 3450 (w), 3090 (w), 2490 (vs), 1425 (m), 1415 (m), 1275 (m), 1150 (m), 1110 (s), 1070 (s), 1045 (w), 1020 (m), 1015 (m), 988 (m), 938 (w), 882 (m), 844 (s), 720 (w), 688 (m) cm^{-1}.

The silica gel was then extracted with CH_3CN, yielding a deep green solution. Removal of CH_3CN followed by addition of H_2O, filtration, and addition of excess $(CH_3)_4NCl$ produced a green precipitate. The precipitate (150 mg) was dissolved in acetone and stripped onto silica gel and chromatographed on a 2 × 15 cm silica gel column. Elution with CH_2Cl_2 removed impurities while elution with 10% acetone/CH_2Cl_2 eluted the green band. Addition of 1-propanol to the filtrate followed by slow rotary evaporation produced 84 mg (1.6%) of dark green crystals of II, $[(CH_3)_4N][C_5H_5FeC_2B_9H_{11}FeC_2B_9H_{11}]$, mp >300 °C. Anal. Calcd for $C_{13}H_{39}B_{18}Fe_2N$: C, 30.28; H, 7.62; B, 37.73; Fe, 21.66; N, 2.72. Found: C, 30.17; H, 7.76; B, 36.51; Fe, 21.74; N, 2.69. Infrared spectrum (Nujol mull): 3100 (w), 2500 (vs), 1490 (s), 1425 (m), 1290 (w), 1155 (w), 1125 (w), 1070 (m), 1060 (w), 1035 (m), 1025 (m), 995 (m), 977 (m), 950 (m), 883 (m), 860 (w), 840 (s), 760 (m), 740 (m), 724 (m) cm^{-1}.

Polyhedral Expansion of 1-(η^5-C_5H_5)-1-Fe-2,3-$C_2B_8H_{10}$. This reaction was performed as above with 0.98 g (4.06 mmol) of 1,2,3-$C_5H_5FeC_2B_8H_{10}$. To the reduced solution was added, as a solid, 6.5 g (19 mmol) of $[C_5H_5FeC_6H_6][PF_6]$. The mixture was stirred 120 h under nitrogen and worked up as above. Elution of the chromatography column with hexane produced ferrocene, and elution with 20% CH_2Cl_2–hexane yielded 60 mg of starting material. A red band eluted in CH_2Cl_2. Addition of a small amount of hexane followed by rotary evaporation of the solvent produced 90 mg of red-purple crystals, mp >310 °C, whose mass and ^1H NMR spectra were consistent with the formulation $(C_5H_5Fe)_2C_2B_8H_{10}$. No 80.5-MHz ^{11}B NMR spectrum was observable for the paramagnetic species. The elemental analysis and magnetic susceptibility were close to that expected for $C_5H_5FeC_2B_8H_{10}$, due presumably to solid-state decomposition.

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Registry No. I, 65915-58-4; II, 65915-60-8; III, 65915-57-3; 3,1,2-$C_5H_5FeC_2B_9H_{11}$, 37185-23-2; 1,2,3-$C_5H_5FeC_2B_8H_{10}$, 42769-15-3; $(C_5H_5Fe)_2C_2B_8H_{10}$, 65982-53-8.

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Porphyrin Intercalation in Mica-Type Silicates

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This paper reports the reactions of *meso*-tetraphenylporphyrin ($TPPH_2$) with selected cations on the interlamellar surfaces of montmorillonite, a swelling layer lattice silicate related to mica. Strongly acidic hydrated Fe^{3+} and VO^{2+} ions react quantitatively with the free base porphyrin to afford the protonated porphyrin dication ($TPPH_4{}^{2+}$) in the form of intercalated monolayers. Monolayers of $TPPH_4{}^{2+}$ are also formed by reaction of the free base porphyrin with hydronium ions on the silicate surfaces. Weakly acidic hydrated Na^+ and Mg^{2+} on the surface-exchange sites afford only trace amounts of $TPPH_4{}^{2+}$. No porphyrin dication is formed with $(n\text{-}C_3H_7)N^+$. Co^{2+}, Cu^{2+}, and Zn^{2+} react to give mainly metalloporphyrin in solution and a hydronium-exchange form of the silicate. Only a small fraction of the neutral metalated porphyrin remains physically adsorbed to the silicate layers. The Bronsted acidity of hydrated cations is further demonstrated by the surface-catalyzed reactions of benzaldehyde and pyrrole. All of the above cations with the exception of $(n\text{-}C_3H_7)_4N^+$ form an intercalated porphyrin intermediate from the aldehyde and pyrrole in aqueous solution. The intermediate, which forms $TPPH_2$ and $TPPH_4{}^{2+}$ when desorbed from the silicate surface, is believed to be a porphomethene or -dimethene. The importance of this latter reaction as a possible mechanism for the prebiotic formation of porphyrins is briefly discussed.

Introduction

Montmorillonite and related swelling mica-type compounds are capable of intercalating a variety of guest molecules between their negatively charged silicate sheets. The formation of coordination complexes with metal-exchange ions on the interlamellar surfaces is among the more common mechanisms available for substrate binding. Although much remains to be learned concerning the coordination chemistry of metal ions on the interlayer surfaces, recent studies[1] suggest that certain complexes retain their solution-like mobility and constitution in the intercalated state, even to the extent of being able to catalyze solution-like reactions in the solid state.[2]

In the present study we have examined the reactions of *meso*-tetraphenylporphyrin with hydrated metal ions in the

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interlayers of montmorillonite. Several earlier reports have indicated that porphyrins bind strongly to layered silicate surfaces. Model studies of the role of porphyrins in petroleum diagenesis have shown that various types of free base porphyrins can bind and undergo transalkylation reactions on montmorillonite under simulated geological conditions.[3] Also, chlorophyllin has been found to bind to layered silicates,[4] and hemin has been intercalated as the hemin cation in montmorillonite.[5] The intercalation of metalloporphyrins in layered silicate structures could be of some interest for solid-state dioxygen binding and catalytic applications. Intercalation of an Fe(II) porphyrin, for example, might permit dioxygen bonding to the complex but inhibit its bimolecular oxidation to the μ-oxo Fe(III) dimer.

The results reported here show in part that porphyrin intercalation can occur but that the species formed is the diprotonated porphyrin cation, not a metalloporphyrin. The exceptional Bronsted acidity found for certain interlayer hydrated metal ions prompted us to investigate the surface-catalyzed condensation of pyrrole and benzaldehyde in aqueous solution. This latter reaction has merit as a possible mechanism for the prebiotic formation of porphyrins.

Experimental Section

Montmorillonite Cation Exchange. Natural sodium montmorillonite (Wyoming) with a particle size <2 μ and a cation-exchange capacity of ca. 92 mequiv/100 g was obtained from American Colloid Co., Skokie, Ill. The more dense fraction of the sample was removed by sedimentation of a 2% slurry in methanol–water. Various cation-exchange forms of the mineral were prepared by adding to the suspended fraction an excess of the chloride salt of the desired metal ion, except in the case of VO^{2+} where the sulfate salt was used. The suspensions were stirred for 24 h at room temperature to allow for complete cation exchange. The mineral was then filtered off, washed free of excess salt, and, except in the case of VO^{2+}-montmorillonite, allowed to dry overnight in air. At 50% relative humidity, the drying procedure resulted in complete displacement of interlayer methanol by water, as judged from IR spectra. In the case of VO^{2+}-montmorillonite, drying in air causes the characteristic blue of hydrated VO^{2+} to be lost and a yellow-green color to develop. The blue color is not restored upon resuspending the mineral in water. Therefore, the VO^{2+}-exchange form was stored under methanol–water and then filtered off and used as needed in the wet, blue state.

$(n\text{-}C_3H_7)_4N^+$-montmorillonite was prepared according to the above procedure by using the bromide salt of the cation. The hydrogen-exchange form was prepared by stirring for 1 h 2.0 g of Na^+-montmorillonite and a 12-fold excess (5.0 g) of the acid form of Dowex 50W-X8, 20–50 mesh resin in 300 mL of ethanol. The mineral was separated from the resin by passing the mixture through a stainless steel screen filter. This procedure minimizes the bulk of hydrogen ion concentration available for reaction with the aluminosilicate framework of the mineral. Since hydrogen ions in the interlayers of montmorillonite are known to be replaced by Al^{3+} ions which migrate slowly out of the aluminosilicate lattice,[6] the hydrogen-exchange form was used immediately after preparation.

The *meso*-tetraphenylporphyrin dication ($TPPH_4^{2+}$) exchange form of montmorillonite was prepared by reaction of H^+-montmorillonite with $TPPH_2$ in acetone or by cation exchange of Na^+- or Cu^{2+}-montmorillonite with $TPPH_4^{2+}$ in glacial acetic acid.

***meso*-Tetraphenylporphyrin.** This compound, containing ca. 3 wt % tetraphenylchlorin as an impurity, was prepared by modification of the procedure described by Adler et al.[7] Freshly distilled pyrrole (3.6 mL, 52 mmol) and freshly distilled benzaldehyde (5.4 mL, 52 mmol) were added to 250 mL of refluxing propionic acid. After a reaction period of 1 h, the mixture was allowed to cool overnight to room temperature. Filtration yielded purple crystals which were washed several times with methanol and then dried at 110 °C for 2 h.

Montmorillonite–$TPPH_2$ Reactions. In a typical experiment a 500 mg sample of homoionic montmorillonite containing ca. 0.45 mequiv of exchangeable cations was added to 10 mg (0.016 mmol) of $TPPH_2$ dissolved in 500 mL of reagent grade acetone at room temperature. The loss of $TPPH_2$ and/or the formation of metalloporphyrin in the solution phase was followed spectroscopically over a 24-h period by observing changes in the intensities of absorption peaks in the UV–visible region. The reaction mixture was then filtered, and the mineral was washed several times with acetone and then dried overnight in air.

Pyrrole–Benzaldehyde Reactions. Five grams (ca. 4.5 mequiv) of homoionic montmorillonite was added to 300 mL of distilled water, and then enough freshly distilled pyrrole and freshly distilled benzaldehyde was added to make the exchange cation:pyrrole:benzaldehyde molar ratio equal to 1:2:2 or 1:1:1. The reaction mixture was allowed to stir for 24 h, during which time the mineral fraction gradually changed to pale pink and then to deep purple. The elapsed time before the initial appearance of the pale pink color was dependent on the nature of the cation occupying the exchange sites of the mineral. The color changes occurred in all cases except for $(n\text{-}C_3H_7)_4N^+$-montmorillonite which gave no evidence for reaction. At the end of the reaction period the mineral products were recovered by freeze-drying.

The surface reaction of aqueous pyrrole and benzaldehyde with Zn^{2+}- and Cu^{2+}-montmorillonite was also carried out under oxygen-free conditions. The reagents were distilled under a nitrogen atmosphere, and all transfers were carried out in a glovebox. The same color changes observed under aerobic conditions were also noted under oxygen-free conditions. Exposure to the atmosphere after freeze-drying the products did not produce any changes in their visible absorption spectra.

Partial desorption of the mineral-bound products could be achieved by three methods: (A) ion-exchange reaction between the freeze-dried product and $(n\text{-}C_3H_7)_4N^+$, (B) Soxhlet extraction of the freeze-dried products with pyridine for 16 h, and (C) ion exchange between $(n\text{-}C_3H_7)_4N^+$ and the mineral-bound product as it is being formed in the reaction mixture. Method A involved stirring for 24 h 72 mg of product and 150 mg of $[(n\text{-}C_3H_7)_4N]Br$ in 100 mL of distilled water, extracting the aqueous phase with benzene, and then drying the benzene solution over Na_2SO_4. Method C was used to desorb product from the H^+-, Cu^{2+}-, and Fe^{3+}-montmorillonite reaction systems. $[(n\text{-}C_3H_7)_4N]Br$ (12 g, 45 mmol) was added at the initial stages of reaction, and the reaction was allowed to continue for 24 h as described above. The reaction mixture was freeze-dried and the residue was extracted with chloroform. The yields of $TPPH_2$ were determined from the intensity of the Soret absorption (ϵ 450 × 10^3 L/(cm mol)). For the reactions of benzaldehyde and pyrrole on Cu^{2+}-montmorillonite, the yields of $TPPH_2$ using desorption methods A, B, and C were ~2%, 4–5%, and 10–12%, respectively.

Porphyrin Intermediates. Intermediates related to those formed by reaction of pyrrole and benzaldehyde on montmorillonite were also prepared in homogeneous solution. Distilled pyrrole (0.20 mL, 2.7 mmol) and benzaldehyde (0.30 mL, 2.7 mmol) were dissolved in 250 mL of chloroform containing one drop of concentrated HCl as catalyst. The reaction mixture was allowed to stir open to the atmosphere. After a reaction time of 1 h at room temperature, the mixture was purged with argon to retard further oxidation, and the visible absorption spectrum of the product in solution was recorded. Attempts to isolate the intermediate in powder or crystalline form were unproductive. The reaction solution was divided into two parts and 1.0 g each of $(n\text{-}C_3H_7)_4N^+$- and Cu^{2+}-montmorillonite was added. Each mixture was allowed to stir under nitrogen for 16 h. Filtration yielded purple-brown minerals in both cases.

Physical Measurements. Electronic absorption spectra were recorded on a Cary 17 spectrophotometer using Nujol mulls of solids mounted between quartz disks and 1-cm path length cells for solutions. Infrared spectra were obtained with a Perkin-Elmer Model 237B grating infrared spectrophotometer. Solid samples were recorded as thin films supported between KBr plates. Electron spin resonance spectra of random powder samples were recorded by use of a Varian E-4 X-band ESR spectrometer. The 001 basal spacings for the various montmorillonite samples were recorded by use of a Philips x-ray diffractometer and Ni-filtered Cu Kα radiation.

Results

$TPPH_2$–Metal Ion Reactions. In the case of montmorillonite we are dealing with a layered silicate with an idealized unit cell formula of $[M^{n+}{}_{0.66/n}\cdot xH_2O][Al_{3.34}, Mg_{0.66}](Si_{8.00})O_{20}(OH)_4$, where M^{n+} is the interlayer exchange cation and x depends on the partial pressure of water in equilibrium with the solid phase. Small amounts of iron substituted for alu-

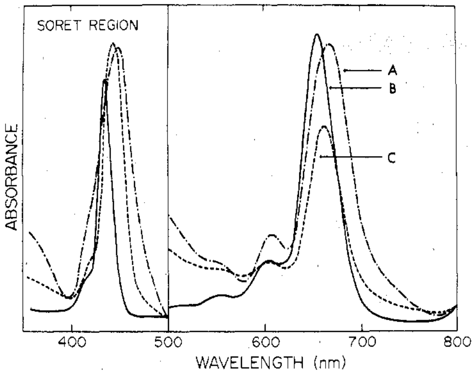


Figure 1. Electronic absorption spectra of (A) $TPPH_2$ bound to Fe^{3+}-montmorillonite, (B) $TPPH_4{}^{2+}$ in glacial acetic acid solution, and (C) $TPPH_4{}^{2+}$-montmorillonite. The absorption scale is in arbitrary units.

minum in octahedral positions and of aluminum substituted for silicon in tetrahedral positions of the oxygen framework are omitted from the formula. From the *a* and *b* parameters of the idealized unit cell ($a \simeq 5.21$, $b = 9.02$ Å), the interlamellar surface area per cation equivalent is ca. 71 Å^2. This means that the average distance between M^{n+}-exchange ions is ca. 8.4, 11.9, or 14.5 Å for $n = 1$, 2, or 3, respectively.

If *meso*-tetraphenylporphyrin, its dication, and metallo complexes are taken to have square shapes and an approximate surface area of 300 Å^2, then each of these species in the intercalated state would cover ~6.4 unit cells or an area equivalent to that occupied by ~4.2 units of silicate charge. Although some reactions between intercalated metal ions and $TPPH_2$ were carried out at cation-exchange equivalent:$TPPH_2$ ratios of 4:1 and less with qualitatively similar results, all of the systems discussed below were investigated at a ratio of 28:1. The latter ratio provides ~2000 Å^2 of basal surface per porphyrin moiety or an interporphyrin distance of ~45 Å. This interporphyrin distance was selected in order to facilitate intercalation and avoid diffusional problems which might otherwise be encountered in attempting to achieve complete monolayer coverage of the interlayer surfaces.

VO^{2+} and Fe^{3+}. The addition of VO^{2+}- or Fe^{3+}-montmorillonite to $TPPH_2$ in acetone solution results in almost complete adsorption of the porphyrin within a few hours at room temperature. The four free base porphyrin bands at 510, 545, 588, and 645 nm are lost and no new bands appear in the solution phase after a reaction period of 25 h. At the initial stages of reaction both exchange forms of the mineral adopt a bright green color and this color is retained throughout the reaction and after filtration and air-drying.

The absorption spectrum of the porphyrin species bound to Fe^{3+}-montmorillonite is shown in Figure 1A. A similar spectrum was obtained for $TPPH_2$ on VO^{2+}-montmorillonite. Comparison of this spectrum with those for the *meso*-tetraphenylporphyrin dication ($TPPH_4{}^{2+}$) in glacial acetic acid and for the $TPPH_4{}^{2+}$-exchange form of montmorillonite (Figure 1B and C, respectively) indicates that the porphyrin binds to Fe^{3+} and VO^{2+} as the diprotonated cation. The overall reaction shown by eq 1, wherein the bars identify surface or intercalated species, must involve the hydrated cation acting as a Bronsted acid.

$$\underline{\overline{2M(H_2O)_x{}^{n+}}} + TPPH_2 \rightarrow \underline{\overline{2M(H_2O)_{x-1}(OH)^{(n-1)+}}} + \underline{\overline{TPPH_4{}^{2+}}} \qquad (1)$$
$$M = VO^{2+}, Fe^{3+}$$

It is noteworthy that bathochromic shifts of 10–15 nm occur in the Soret band near 435 nm and band I near 655 nm upon binding of $TPPH_4{}^{2+}$ to the silicate surfaces. These shifts suggest that the porphyrin ring and phenyl groups tend toward a more coplanar conformation in the surface-bonded state.

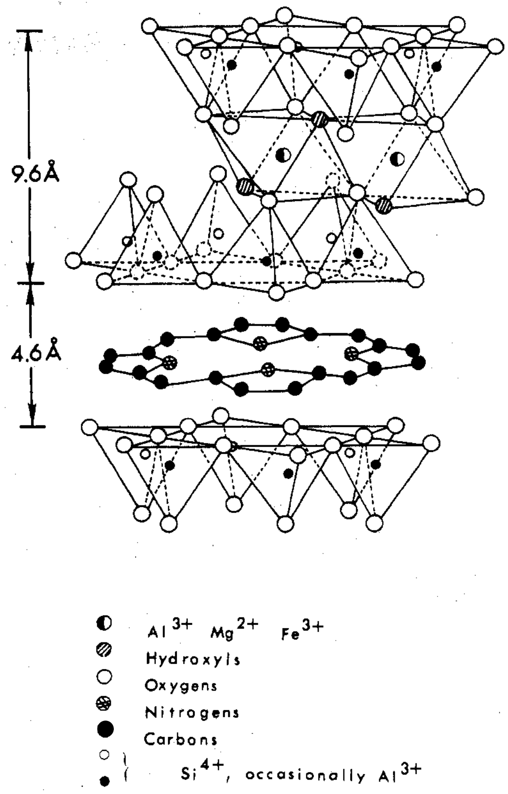


Figure 2. Schematic illustration of the $TPPH_4{}^{2+}$ porphyrin nucleus oriented in the interlayers of montmorillonite. Protons and phenyl groups are omitted for clarity.

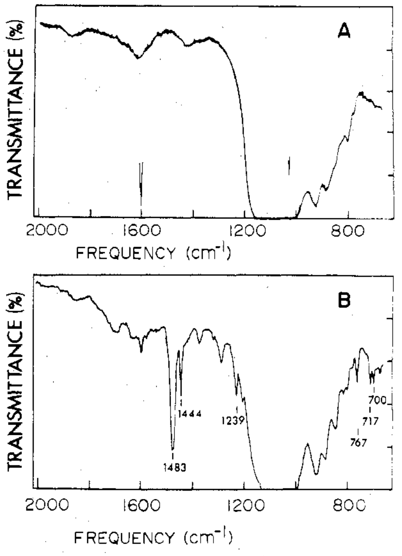


Figure 3. Infrared spectra of (A) Na^+-montmorillonite and (B) $TPPH_4{}^{2+}$-montmorillonite. Both samples were dried in air at 110–130 °C to facilitate desorption of interlayer water and acetone.

Intercalation of $TPPH_4{}^{2+}$ with the mean plane of the porphyrin ring parallel to the silicate sheets (as illustrated in Figure 2) is evident from x-ray diffraction data. A 001 basal reflection of 14.2 Å is observed for $TPPH_4{}^{2+}$-saturated montmorillonite. Because the basal spacing is ca. 9.6 Å when no interlamellar species are present, the separation between the silicate sheets is ca. 4.6 Å, which is the approximate thickness of the porphyrin nucleus.[8] Infrared absorption data also support the planar orientation of $TPPH_4{}^{2+}$ in the interlayer region (Figure 3). The bands at 1483, 1444, and 1239 cm^{-1} are near those previously reported for $TPPH_4{}^{2+}$.[9] The bands at 767, 717, and 700 cm^{-1} are assigned to C–H deformations characteristic of mono-substituted benzene.[10] The 717- and

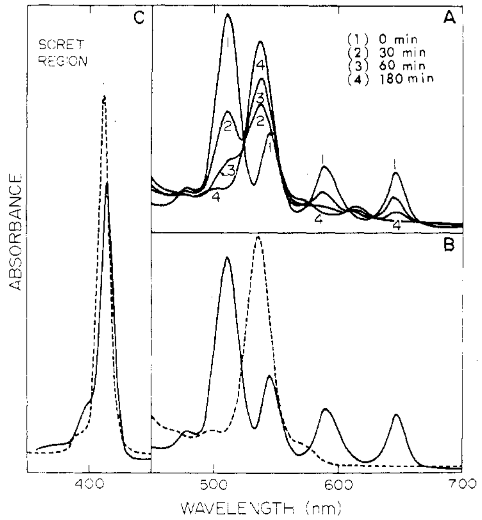


Figure 4. (A) Spectrophotometric changes which occur in $TPPH_2$–acetone solutions after addition of Cu^{2+}-montmorillonite. Regions B and C show the visible and Soret bands before (—) and 24 h after (- - -) the reaction was initiated at 25 °C. The absorbance scale is in arbitrary units.

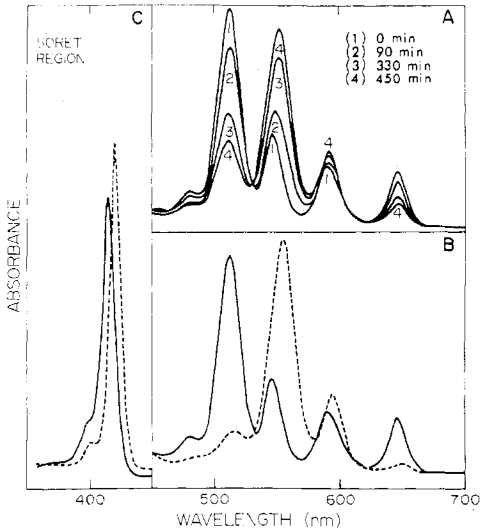


Figure 5. (A) Spectral changes which occur in $TPPH_2$–acetone solutions upon reaction with Zn^{2+}-montmorillonite. Regions B and C show the visible and Soret bands before (—) and 24 h after (- - -) reaction initiated at 25 °C. Absorbance scale is in arbitrary units.

700-cm^{-1} bands exhibit significant pleochroism when the plane of an oriented film sample is inclined relative to the path of the infrared beam. The band at 700 cm^{-1} decreases in the intensity while the band at 717 cm^{-1} gains in intensity. These pleochroic effects indicate a preferred orientation of the phenyl groups relative to silicate sheets.

Cu^{2+}, Zn^{2+}, and Co^{2+}. As shown in Figure 4, the reaction of $TPPH_2$ in acetone with Cu^{2+}-montmorillonite leads to the gradual replacement of free base porphyrin bands by new solution bands at 538, 500, and 570 nm characteristic of Cu(TPP).[11,12] The Zn^{2+}-montmorillonite–$TPPH_2$ reaction behaves similarly with the 515-, 553-, and 593-nm bands of Zn(TPP)[11] replacing those of $TPPH_2$ (Figure 5). It should be remarked that not all absorption traces in Figures 4 and 5 pass through isosbestic points because of scattering caused by finely divided mineral particles which remain suspended after centrifuging.

The spectral data clearly show that metalation of the porphyrin occurs on the mineral surfaces, but the neutral complex is readily desorbed. In the case of Cu^{2+}, spectral and chemical analyses indicate that at least 95% of the porphyrin is converted to soluble Cu(TPP) and less than 5% is bound to the silicate surface as $TPPH_4^{2+}$. Thus, the overall reaction between intercalated Cu^{2+} or Zn^{2+} and $TPPH_2$ can be written as

$$\overline{M(H_2O)_x^{2+}} + TPPH_2 \rightarrow \overline{2H_3O^+} + M(TPP) \qquad (2)$$

$$M = Cu, Zn$$

This overall reaction is preceded by a Bronsted acid–base equilibrium between the hydrated metal ion and $TPPH_2$ (cf. eq 1). At the initial stages of reaction the mineral phase adopts the characteristic green of $TPPH_4^{2+}$, but the color is lost as reaction 2 progresses.

The interlayer protons formed in reaction 2 are available for further reaction with $TPPH_2$. At a Cu^{2+}:$TPPH_2$ molar ratio of 1:2, all of the copper appears in solution as Cu(TPP). Approximately half of the resulting intercalated protons react further with excess $TPPH_2$ to form $TPPH_2^{2+}$ (eq 3). The

$$\overline{2H_3O^+} + TPPH_2 \rightarrow \overline{TPPH_4^{2+}} \qquad (3)$$

number of surface protons which react according to eq 3 appears to be determined solely by size factors. As noted earlier, an intercalated porphyrin dication is expected to occupy a surface area of ca. 300 Å^2, or an area equivalent to ca. 4.2 units of silicate charge. Since each porphyrin cation can neutralize only two charge units, the remaining 2.2 charge sites must be balanced by protons. In the presence of a close-packed monolayer of $TPPH_4^{2+}$, these protons can be accommodated in the hexagonal oxygen cavities of the silicate framework (cf. Figure 2).

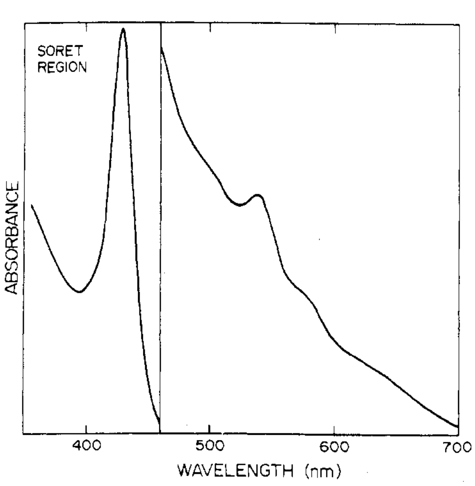


Figure 6. Absorption spectrum of Co(TPPH) physically adsorbed on the external surface of Co^{2+}-montmorillonite. The complex was formed by reaction of $TPPH_2$ in acetone with Co^{2+}-montmorillonite at 25 °C. Absorbance is in arbitrary units.

The reaction of Co^{2+}-montmorillonite with $TPPH_2$ in acetone at room temperature affords a yellow-tan solid phase containing a trace amount (<1%) of bound Co(TPP). The spectrum of this species is shown in Figure 6. The Soret band at 429 nm and the visible band at 538 nm are red-shifted 10–20 nm from those observed for the Co(TPP) in solution. Because of the small amount of Co(TPP) present, it is not possible to determine by x-ray powder diffraction methods whether the complex is intercalated. The observed 001 spacing of 12.6 Å for the mineral dried at 110 °C is in agreement with the value expected for uncomplexed cobalt(II) in the interlayers.

Attempts to observe intercalation of Co(TPP) by increasing the reaction temperature to 56 °C and adding excess $TPPH_2$ led instead to Co(TPP) in solution and a bright green solid phase characteristic of $TPPH_4^{2+}$-montmorillonite. The spectral changes which result from reaction of $TPPH_2$ in acetone and

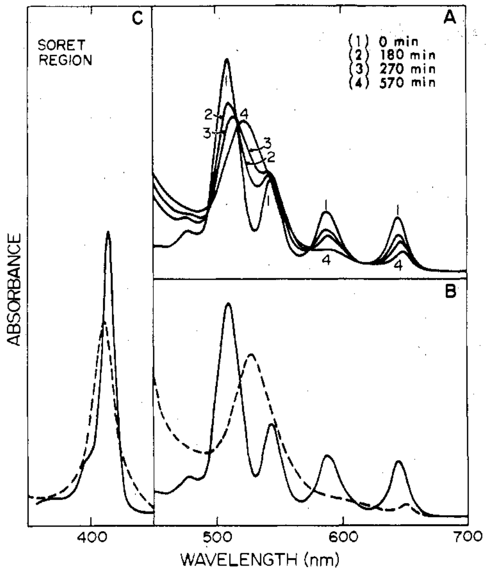


Figure 7. (A) Spectral changes which occur in acetone solutions of $TPPH_2$ upon reaction with Co^{2+}-montmorillonite at 56 °C. Regions B and C are the visible and Soret regions before (—) and 24 h after (- - -) reaction. Absorbance scale is in arbitrary units.

Co^{2+}-montmorillonite at reflux temperature are shown in Figure 7. These data indicate that surface metalation and subsequent desorption occurs as in the case of Cu^{2+} and Zn^{2+}, but the reaction is slower.

Mg^{2+}, Na^+, and $(n\text{-}C_3H_7)_4N^+$. Very small decreases in free base porphyrin absorptions are observed upon reaction of $TPPH_2$ with Mg^{2+}- or Na^+-montmorillonite. In both cases, the mineral phase adopts a pale green color, which indicates that a small amount of $TPPH_2$ is bound as the dication. The protonation reaction is attributed to partial hydrolysis of the metal ions on the silicate surfaces as found for VO^{2+} and Fe^{3+}, except that the equilibrium expressed by eq 1 lies far to the left in the case of M = Mg^{2+} and Na^+. No reaction occurs with free base porphyrin when $(n\text{-}C_3H_7)_4N^+$ ions occupy the exchange sites of the silicate structure.

Benzaldehyde–Pyrrole Reactions. The protonation of $TPPH_2$ by hydrated metal ions in the interlayers of montmorillonite indicates that the acid dissociation constants of the metal ions are appreciably larger on the silicate layers than in aqueous solution. This observation prompted us to attempt the surface-catalyzed synthesis of $TPPH_2$ from benzaldehyde and pyrrole in aqueous media. Aldehydes and pyrrole are known to afford porphyrins only under strongly acid conditions.[13a] Although the pH values of montmorillonite suspensions are in the range 3.0–9.5 where little or no porphyrin can be formed in homogeneous solution, we expected the surface-catalyzed condensation of adsorbed benzaldehyde and pyrrole.

The addition of equimolar amounts of freshly distilled pyrrole and benzaldehyde to an aqueous slurry of Fe^{3+}-, VO^{2+}-, Cu^{2+}-, H^+-, Co^{2+}-, Zn^{2+}-, Mg^{2+}-, or Na^+-montmorillonite yields a dark purple mineral phase. Reaction on the silicate surfaces occurs whether the reagents are mixed in the presence or absence of oxygen. The reaction is complete within minutes for the most acidic cations (H^+, VO^{2+}, Fe^{3+}) and within 3 h for the less acidic ions. The weakly acidic surfaces of $(n\text{-}C_3H_7)_4N^+$-montmorillonite fail to form a purple complex even after a reaction time of 24 h. At the exchange ion:pyrrole:aldehyde ratios employed, 1:2:2 for M^{2+} and M^{3+} ions or 1:1:1 for M^+ ions, sufficient montmorillonite is present to permit complete adsorption of pyrrole and benzaldehyde on the interlayer surfaces.

The purple species formed in each metal ion system exhibits an intense absorption in the region 506–522 nm. A typical spectrum for the bound product obtained with Cu^{2+}-montmorillonite is shown in Figure 8A. Partial desorption of the product can be achieved by treatment with chloroform, with pyridine, or, better, with chloroform containing $(n\text{-}C_3H_7)_4N^+$ as an exchange cation. Allowing the desorbed product to age in solution at room temperature results in the formation of $TPPH_2$ and $TPPH_4^{2+}$. This result indicates the purple product is a porphyrin intermediate. Spectra of the chloroform–$[(n\text{-}C_3H_7)_4N]Br$ extract obtained from the Cu^{2+}-montmorillonite reaction are given in Figure 8B and C. The bands at 485, 447, and 415 nm are assigned to the desorbed porphyrin intermediate, $TPPH_4^{2+}$, and $TPPH_2$, respectively. It is seen that the intensities of the Soret bands for $TPPH_4^{2+}$ and $TPPH_2$ increase at the expense of the intermediate band. The shift in position of the intermediate band from 512 nm in the surface-bonded state to 485 nm in chloroform solution is similar to the behavior shown by $TPPH_4^{2+}$ (vide supra). X-ray basal spacings show that the intermediate is intercalated between interlayers 5.1 Å thick.

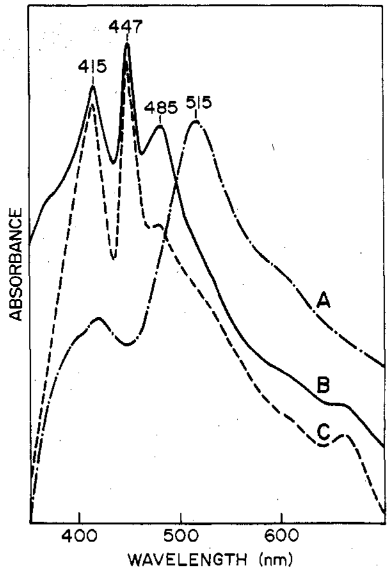
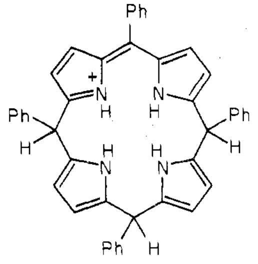


Figure 8. (A) Nujol mull spectrum of the purple product formed on the interlamellar surfaces of Cu^{2+}-montmorillonite by reaction of adsorbed benzaldehyde and pyrrole. A blank sample of the mineral was placed in the reference beam to partially compensate for scattering. (B, C) Spectra of the porphyrin products obtained by desorption of the intermediate in $CHCl_3$ containing $(n\text{-}C_3H_7)_4N^+$ as an exchange cation. Spectrum B was recorded after 2 h at 25 °C; spectrum C, after 24 h.

An intermediate absorbing near 500 nm has been observed previously during the oxidation of porphyrinogens to porphyrins in homogeneous solution.[13-15] Mauzerall[14b,c] and Dolphin[15] have argued that the band probably arises from the presence of a dipyrrolemethene chromophore in a porphomethene or porphodimethene structure. The porphomethene and porphodimethene possible in the reaction of benzaldehyde and pyrrole are shown in structures **1a** and **1b**, respectively. The dipyrrolemethene chormophore is identified in structure **1c**.

In an attempt to verify a porphomethene or -dimethene intermediate in the condensation–oxidation of pyrrole and benzaldehyde on the interlayer surfaces of montmorillonite, we have formed the intermediate in homogeneous solution and then allowed it to adsorb on the surfaces of Cu^{2+}-montmorillonite. As shown in Figure 9A, a species with λ_{max} 477 nm is obtained by reaction of benzaldehyde and pyrrole in chloroform containing a drop of aqueous HCl as catalyst. The spectrum of its final oxidation products $TPPH_4^{2+}$ (λ_{max} 477, 660 nm) and $TPPH_2$ (λ_{max} 415 nm) is shown in Figure 9B. Adsorption of the intermediate from chloroform solution onto Cu^{2+}-montmorillonite affords a purple mineral with the



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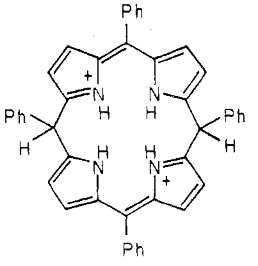
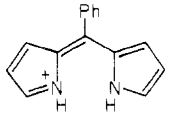


1b



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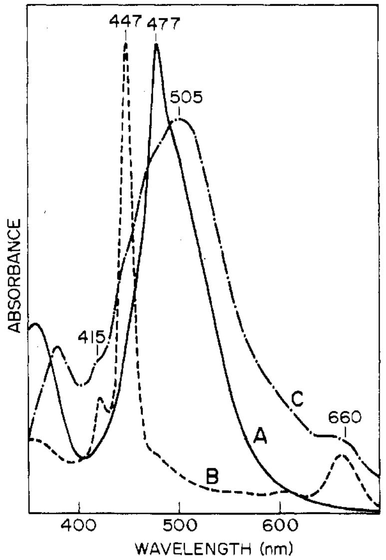


Figure 9. (A) Spectrum of the porphyrin intermediate obtained by reaction for 2 h of 1.1 × 10^{-2} M benzaldehyde and pyrrole in $CHCl_3$ containing as catalysts 0.1 mL of concentrated HCl per 250 mL of solution. The reaction was carried out at 25 °C in the presence of air. (B) Spectrum of the porphyrin products obtained after a reaction time of 24 h. (C) Mull spectrum of the intermediate formed in $CHCl_3$ and then adsorbed onto the external surfaces of Cu^{2+}-montmorillonite.

spectrum shown in Figure 9C. The position of the band for the adsorbed intermediate (λ_{max} 505 nm) is near that observed for the intermediate formed by reaction of benzaldehyde and pyrrole in the interlayers (λ_{max} 512 nm; cf. Figure 8A). The difference in band positions, as well as bandwidth, may be related to a difference in the mode of surface binding. Adsorption of the intermediate from chloroform solution onto Cu^{2+}-montmorillonite involves binding at external surfaces of the crystallite particles ($d_{001} \approx 12.6$ Å) whereas reaction of benzaldehyde and pyrrole in the interlayers results in intercalation ($d_{001} = 14.7$ Å). Since intercalation involves interaction of the intermediate with two silicate layers, rather than with one surface as in external adsorption, there should be a greater tendency toward coplanarity of the phenyl and porphodimethene rings and larger bathochromic shifts in the intercalated state.

Discussion

meso-Tetraphenylporphyrin undergoes two distinct types of reactions with metal ions on the planar silicate surfaces of montmorillonite. One reaction is a Bronsted acid–base reaction between the hydrated cations and the free base porphyrin which affords the diprotonated porphyrin dication, as shown by eq 1. The second reaction involves metalation of the porphyrin ring and subsequent desorption of the metalloporphyrin from the silicate surfaces as expressed by eq 2.

Hydronium ions on the surfaces react with free base porphyrin to form intercalated $TPPH_4^{2+}$ monolayers according to eq 3. The number of porphyrin rings which react with surface hydronium ions is determined by the number of $TPPH_4^{2+}$ ions needed to form a complete monolayer. The visible absorption spectra, infrared pleochroic effects, and the x-ray diffraction results indicate that $TPPH_4^{2+}$ assumes a more planar conformation in the adsorbed state than in the solution state. This suggests that the silicate layers are capable of inducing conformational changes in the structures of porphyrins adsorbed into the interlamellar regions.

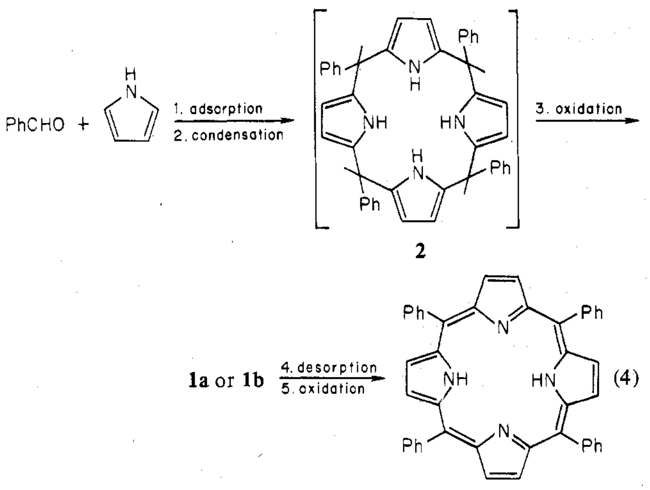
The protonation of $TPPH_2$ by hydrated metal ions is dependent on the metal ion hydrolysis constant. Cations that are acidic in aqueous solution such as Fe^{3+} and VO^{2+} with pK_h values of 2.19 and 4.77, respectively, form intercalated $TPPH_4^{2+}$ quantitatively. Very weakly acidic ions such as Mg^{2+} ($pK_h = 11.4$) and Na^+ ($pK_h = 14.5$) form only trace amounts of $TPPH_4^{2+}$.

Cu^{2+}, Co^{2+}, and Zn^{2+} are the only cations in this study to become incorporated into the porphyrin ring. Dication formation also occurs during metalloporphyrin formation (pK_h = 7.53, 9.6, and 9.6 for Cu^{2+}, Co^{2+}, and Zn^{2+}, respectively), but the metalation reaction predominates. As can be judged from Figures 4, 5, and 7, the order of reactivity toward $TPPH_2$ on the silicate surfaces is $Cu^{2+} > Zn^{2+} >> Co^{2+}$. This same reactivity order for porphyrin metalation is observed in aqueous environments.[16,17] Little or no neutral metalloporphyrin, however, remains bound to the silicate sheets. Trace amounts of physically adsorbed Co(TPP) can be detected spectrophotometrically, but formation of intercalated monolayers does not occur.

Intercalation seems to be restricted to electrostatically bonded cationic porphyrins such as $TPPH_4^{2+}$ and the hemin cation reported previously by Weiss and Roloff.[5] Bivalent metalloporphyrins are known to be catalysts for oxidative dehydrogenation,[18] but their inability to penetrate into and remain bonded to the silicate layers of montmorillonite precludes the use of swelling mica-type silicates as inorganic supports for metalloporphyrin catalysts and reversible oxygen carriers.

Previously reported studies have concluded that hydrated cations are appreciably more dissociated on layered silicate surfaces than in homogeneous solution.[19] Qualitative evidence for enhanced dissociation is provided not only by the protonation of $TPPH_2$ by cations that are weakly acidic in aqueous solution but also by the surface-catalyzed formation of an intercalated porphyrin intermediate from aqueous solutions of benzaldehyde and pyrrole. According to the mechanism proposed by Dolphin[15] for porphyrin formation from pyrrole and aldehydes in acetic or propionic acid, the porphomethene or porphodimethene (**1a** or **1b**) is derived from a porphyrinogen (**2**). Oxidation of the porphyrinogen may involve HO_2^+ when oxygen is present or a free-radical mechanism in absence of oxygen. Further oxidation of the intermediate dimethene affords the porphyrin (**3**). A similar scheme is proposed for the surface-catalyzed formation of $TPPH_2$ from benzaldehyde and pyrrole in aqueous media (eq 4).

It is noteworthy that the abiological synthesis of porphyrins on primative Earth 3.5–4.5 billion years ago has been often postulated to account for the evolution of photosynthesis and respiration in living systems.[20] Attempts to simulate porphyrin synthesis under reasonable geological conditions have met with marginal success. Minute quantities of porphyrin-like molecules (10^{-3}–10^{-4}% yield) have been reported from electrical discharge experiments on NH_3–CH_4–H_2O mixtures[21] and from photochemical and thermal reactions of likely prebiotic aldehydes and pyrrole.[22] The yields of porphyrin obtained in the present study are in the range 2–12%, depending on the



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nature of the interlayer cation and the method used to desorb the porphyrin intermediate from the mineral surface. Layered mica-type silicates such as montmorillonite are ubiquitous products of hydrothermal reactions and the weathering of primary silicate minerals.[23] Also, at least 70 different aldehydes are known[24] to react with pyrrole in acidic media to form porphyrins in yields up to 20%. These facts, together with the 10^3–10^5 times greater yields of porphyrins achieved in this study, prompt us to suggest that the reactions of aldehydes and pyrroles on layered silicate minerals is a much more likely mechanism for the abiological formation of porphyrins than those proposed previously. This model, along with recent reports of polypeptide,[25] polynucleotide,[26] and monosaccharide[27] formation on related mineral surfaces, supports Bernal's[28] original suggestion that adsorptive and catalytic processes on layered silicates may have played an important role in the chemical evolution of biologically importent molecules.

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Registry No. Montmorillonite, 1318-93-0; $TPPH_2$, 917-23-7; $TPPH_4^{2+}$, 50849-35-9; Fe^{3+}, 20074-52-6; VO^{2+}, 20644-97-7; Cu^{2+}, 15158-11-9; Zn^{2+}, 23713-49-7; Co^{2+}, 22541-53-3; Mg^{2+}, 22537-22-0; Na^+, 17341-25-2; benzaldehyde, 100-52-7; pyrrole, 109-97-7.

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Molybdenocene Metallocycles. Alkene and Alkyne Complexes Characterized by Spectroscopic and Chemical Means

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Synthesis of $(C_5H_5)_2Mo(CH_3C{\equiv}CH)$ and an improved synthesis of $(C_5H_5)_2Mo(C_2H_2)$ are reported. In addition to ^1H NMR spectra, decoupled and gated decoupled ^{13}C NMR spectra are reported for these compounds as well as for $(C_5H_5)_2Mo(C_2H_4)$. On the basis of comparisons of these NMR spectra to that of the corresponding carbocycles as well as other evidence, metallocyclic structures are proposed for the olefin and acetylene complexes of molybdenocene. Hydrolysis chemistry of $(C_5H_5)_2MoC_2H_2$, $(C_5H_5)_2Mo(C_2H_4)$, and $(C_5H_5)_2Mo(CH_3C{\equiv}CCH_3)$ is discussed and related to similar nitrogenase enzyme reductions.

Bonding in bis(cyclopentadienyl)metal complexes of olefins and alkynes continues to be a subject of great interest.[1] Descriptions of the nature of the metal–hydrocarbon bonding range from suggestions of π complexes capable of metal–olefin bond rotation to metallocycles as well as intermediate cases.[2-5] Our investigations into molybdenocene chemistry have suggested that its olefin and acetylene complexes act chemically like metallocycloalkanes and metallocycloalkenes,[6] respectively.