CHEMISTRY LETTERS, pp. 1117-1120, 1988.

Intercalation of Co(II) *meso*-Tetrakis(1-methyl-4-pyridyl)porphyrin into Montmorillonite

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The title compound was intercalated into montmorillonite as Co-porphyrin complex by ion exchange in acid solution. Interlamellar distance of montmorillonite expanded from its regular value of 0.27 nm to 0.37 nm upon intercalation. Fluorescence emission and electron absorption revealed the retention of Co in the porphyrin intercalated.

We recently succeeded in the insertion of Co(II) *meso*-tetrakis(1-methyl-4-pyridyl)porphyrin [CoTMPyP] into interlamellar space of montmorillonite [MT]. Since this is the first instance in which metalloporphyrin as such was directly intercalated into clay mineral, we report briefly the method of preparation and evidence in support for the metalloporphyrin insertion.

CoTMPyP was prepared from $Co(CH_3COO)_2$, methyl-p-toluenesulfonate, pyridin-4-aldehyde, and pyrrol according to the method recommended.1) CoTMPyP (20 mg) was dissolved in H_2O (100 ml) to which HNO_3 had been added to adjust acidity of the solution. MT (2 g) was then added to the solution. After being refluxed for 5 h, solid material was recovered by centrifugation/filtration, dried in vacuum, crushed under 100 mesh size, and then subjected to the subsequent characterization.

Electron absorption of CoTMPyP in colloidal solution of saponite [SA] was observed under varying acidity by stopped-flow method and at an ambient temperature. SA was used instead of MT, since the synthetic clay is transparent to the particular light adopted, hence more appropriate for diagnostic studies. Absorption at 432 nm, characteristic of free CoTMPyP, decreased as reaction time elapsed. And, instead, a new absorption emerged at 450 nm (Fig.1). In our separate study, the 450 nm band was found characteristic of SA digested with neutral CoTMPyP solu-

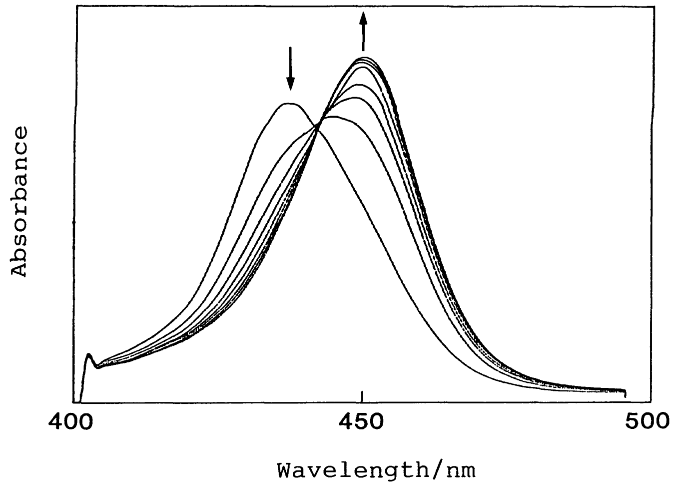

Fig.1. Absorption spectra of CoTMPyP in colloidal SA solution measured every 40 ms in the range between 20 ms and 300 ms.

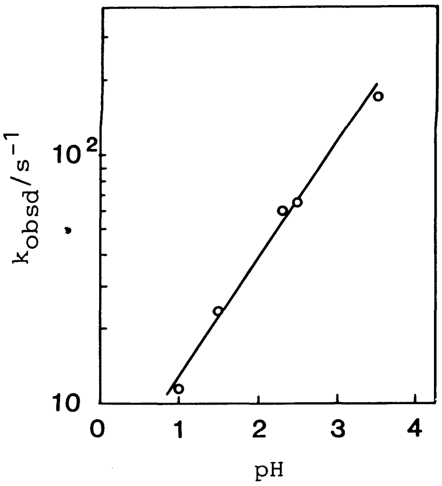

Fig.2. Relation between k_{obsd} and pH.

tion. X-Ray diffraction of the SA so treated revealed 0.3 nm for its interlamellar distance. Since the distance is too short to accommodate CoTMPyP, the 450 nm band is ascribed to CoTMPyP adsorbed on the exterior surface of SA. The adsorption rate constant, k_{obsd}, calculated from the spectral change and the hypothetical first order kinetics, increased linearly with pH of the solution (Fig.2). Extension of the reaction time beyond 500 ms, however, resulted in the gradual decrease in the 450 nm band intensity and, in turn, a still new absorption emerged at 465 nm (Fig.3).

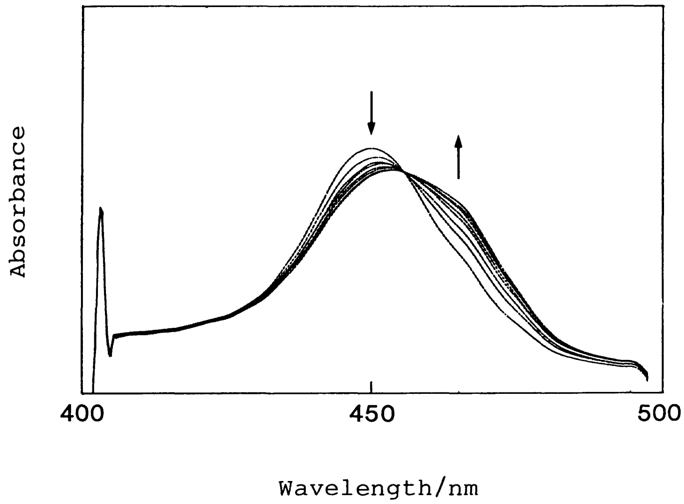

Fig.3. Absorption spectra of CoTMPyP in colloidal SA solution measured every 2 s in the range between 1.05 s and 15.05 s.

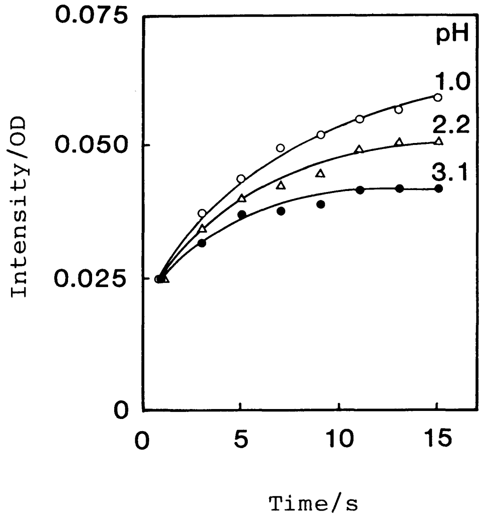

Fig.4. Absorbance of 465 nm band.

In our separate study, the 465 nm band was found characteristic of SA digested with acidic CoTMPyP solution. Since the interlamellar distance of 0.53 nm determined by X-ray diffraction with the SA so treated is sufficient to accommodate CoTMPyP, the 465 nm band is ascribed to CoTMPyP intercalated in SA. In about 15 s, the intensity of the latter band leveled off and approached to quasi-steady values depending on pH of the solution (Fig.4). The approach was made considerably faster when the solution was refluxed. Thus, higher pH favored the adsorption whereas lower pH favored the intercalation.

The X-ray diffraction study was extended to MT itself and to MT treated in a variety of conditions. Results are summarized in Table 1 in which values listed in column 3 are those corrected for the thickness of silicate layer of 0.96 nm. In an agreement with existing data,[2)] distance of 0.27 nm was deduced for our fresh MT (Entry A). Digestion of the fresh MT with H_2O (Entry B) and with HNO_3 (Entry C) resulted in an expansion, probably due to an inclusion of H_2O. Result was much the same when MT was digested with aqueous CoTMPyP (Entry D), excepting that the color characteristic of porphyrin faded away quickly. CoTMPyP may be adsorbed on the exterior surface of MT in Entry D where anionic sites of MT were available for the adsorption. Contrary to the above, with Entries E and F where anionic sites were presumably protected by protons, the color disappeared with a slower rate and the interlamellar space expanded to the size sufficient to accommodate TMPyP. Note that the thickness of 0.35 nm is estimated for TMPyP, if the angle between porphyrin and methylpyridinium rings is taken as 45 degrees. In these instances, therefore, a slow exchange between protons and cationic porphyrins may take place

Table 1. Interlamellar distance of montmorillonite treated with a variety of conditions

Entry	Treatment	Spacing nm	Amount of porphyrin 10^{-5}mol(g-MT)$^{-1}$
A	Fresh MT	0.27	0
B	MT refluxed in H_2O for 5 h	0.30	0
C	MT refluxed in HNO_3(0.001 M) for 5 h	0.28	0
D	MT refluxed in CoTMPyP/H_2O for 5 h	0.29	1.8
E	MT refluxed in CoTMPyP/HNO_3(0.001 M) for 5 h	0.37	0.54
F	MT refluxed in TMPyP/HNO_3(0.001 M) for 5 h	0.38	1.6

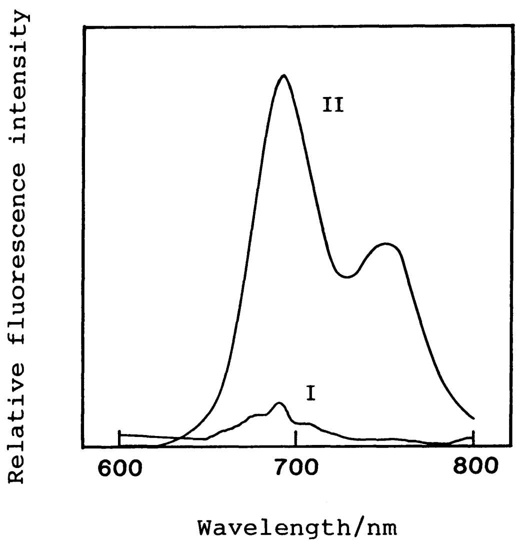

Fig.5. Fluorescence emission spectra.
I:Entries D and E, II:Entry F.

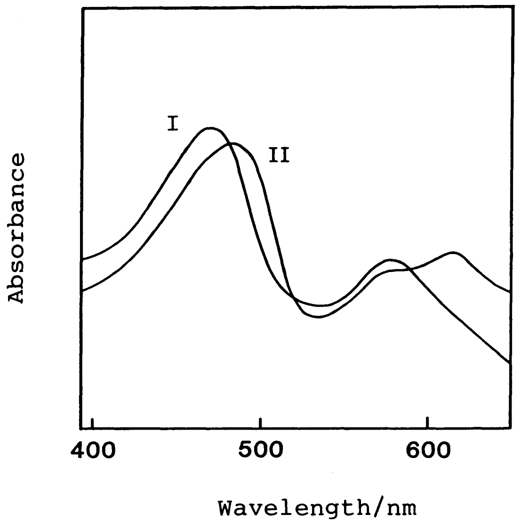

Fig.6. Electron absorption spectra.
I:Entries D and E, II:Entry F.

in the interlamellar space. Values in column 4 (Table 1) are those calculated on the basis of the complete consumption of either CoTMPyP or TMPyP introduced.

Solid products obtained with Entries D, E, and F were tested for their fluorescence emission (600 nm - 800 nm) using excited light of 460 nm (Fig.5). The emission characteristic of TMPyP appeared at 690 nm with Entry F,[4)] whereas there was no such emission with Entries D and E. We, therefore, conclude that CoTMPyP was adsorbed on the external anionic sites of MT in Entry D, and intercalated into MT in Entry E. The same samples were further tested for their adsorption spectra (370 nm - 650 nm) with electron spectrophotometer equipped with an integration sphere (Fig.6). The result indicates essentially the same conclusion. Absorption spectra characteristic of non-metallated TMPyP was observed only with Entry F.[3)] The spectra blue-shifted and the absorption at 614 nm disappeared with Entries D and E, indicating that porphyrin retained its central Co ion.

The present paper demonstrates that the use of cationic metalloporphyrin as a guest complex and the adjustment of ion exchange rate over anionic sites in host lattice are the key to the direct intercalation.

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(Received March 18, 1988)