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Intercalation of Porphyrin (TMPyP) and Copper-Porphyrin into γ-Zirconium Phosphate

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Abstract. Water-soluble $\alpha, \beta, \gamma, \delta$-tetrakis(4-$N$-methylpyridyl)porphine (TMPyP) was directly intercalated into γ-zirconium phosphate (γ-ZrP) with expansion of the interlayer distance from 12.3 to a maximum of 17.2 Å, indicating parallel orientation of porphyrin to the layer of γ-ZrP. Diffuse reflectance spectra of the intercalate shows that the porphyrin is protonated in the interlayer space. Uptake of Cu^{2+} ions into the porphyrin intercalate takes place with further increase in the interlayer distance. It was observed that TMPyP metalated Cu^{2+} in γ-ZrP. Copper porphyrin can also be taken up quite easily and an interlayer spacing of 18.6 Å is attained.

Key words: γ-Zirconium phosphate, porphyrin (TMPyP), copper porphyrin, intercalation

1. Introduction

Extensive studies have been made on the intercalation behavior of organic bases into crystalline layered host materials such as clay minerals and insoluble acid salts of tetravalent metal phosphates. Among them, γ-zirconium phosphate, $ZrPO_4(H_2PO_4)\cdot 2H_2O$ (referred to as γ-ZrP) is known for its large interlayer distance and small free area associated with each active site, compared to α-zirconium phosphate (α-ZrP), one of the most extensively investigated host compounds [1]. In the latter, some pre-swelling of the interlayer space is generally needed in order to incorporate bulky guest species. For TMPyP, pre-intercalation of p-methoxyaniline (PMA) has been successfully carried out by Kim *et al.* for α-ZrP [2]. They showed that water-soluble TMPyP completely converted the PMA pre-intercalated α-ZrP to new phases with an interlayer distance near 17 Å. No data are available on the intercalation of the porphyrins in γ-ZrP, but it was expected that they might be taken up directly from aqueous solution. Thus, in our experience, α-diimines such as 2,2′-bipyridine and 1,10-phenanthroline were directly incorporated into the

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interlayer space of γ-ZrP [3], whereas these α-diimines were not intercalated into α-ZrP unless its layers were pre-swelled by the formation of a metastable ethanol intercalate [4,5].

The present work reveals that TMPyP or CuTMPyP can be incorporated into the interlayer region of γ-ZrP without pre-intercalation. On the other hand, PMA pre-intercalated γ-ZrP fails to convert PMA to TMPyP, and TMPyP is considered to be adsorbed on the crystalline surface. Diffuse reflectance spectra of the intercalates gave some information on protonation or non-protonation of porphyrins in the host matrix under different conditions.

2. Experimental

2.1. MATERIALS

γ-ZrP was synthesized by direct precipitation from fluorozirconate solution as reported previously [3]. The interlayer distance in the hydrogen form was 12.3 Å. TMPyP was obtained as the tetrakis(*p*-toluenesulfonate) from Dojindo Laboratories, and used as received.

2.2. DIRECT INTERCALATION OF TMPyP INTO γ-ZrP

TMPyP(150–300 mg, 0.11–0.22 mmol) was dissolved in 20 mL of deionized water, to which 150 mg (0.47 mmol) of γ-ZrP was added to form a suspension. The mixture was shaken at 25 or 60 °C for 2 or 13 days for three batches of sample solutions. After centrifugation, the solids were washed with deionized water, then air dried. The resulting crystallites (γ-ZrP/TMPyP) were subjected to X-ray powder diffraction measurement (XRD) and elemental analysis. In this article, the expression γ-ZrP/TMPyP as (host/guest) is adopted for an intercalation compound.

2.3. PRE-INTERCALATION OF PMA INTO γ-ZrP AND UPTAKE OF TMPyP

γ-ZrP (200 mg, 0.627 mmol) was suspended in 20 mL of ethanol, and 772 mg (6.27 mmol) of PMA was mixed in the suspension. The mixture was shaken at 40 °C for 2 to 4 days. The suspension was centrifuged, and the solid was washed with ethanol, then air dried. Uptake of PMA was confirmed by XRD and elemental analysis.

Intercalation of TMPyP into the γ-ZrP/PMA intercalate was attempted as follows. A weighed amount (150 mg, 0.11 mmol) of TMPyP was dissolved in 20 mL of water. γ-ZrP/PMA (207 mg, 0.468 mmol) was then added, and the mixture was shaken at 25–30 °C for 2 days. After centrifugation, the solid was washed with (1 : 1) ethanol and air dried. Another run was carried out by using 300 mg of TMPyP at 50 °C for one week.

2.4. UPTAKE OF Cu^{2+} INTO γ-ZrP/TMPyP

γ-ZrP/TMPyP obtained by direct intercalation was employed to incorporate Cu^{2+}. γ-ZrP/TMPyP (130 mg, 0.4 mmol) was suspended in 10 mL of 0.1 mol dm^{-3} copper acetate and the mixture was shaken at 25 °C for 2 days. The amount of Cu^{2+} taken up was determined by EDTA titration of the initial and final solution phases with PAN indicator. The solid phase (γ-ZrP/TMPyP-Cu) was washed with water, air dried and subjected to XRD and diffuse reflectance (DR) spectral measurement. XRD was measured with a Shimadzu XD-610 diffractometer, using Ni-filtered CuK_α radiation. DR spectra were measured with a Hitachi U-3400 spectrophotometer.

2.5. INTERCALATION OF Cu-TMPyP INTO γ-ZrP

Weighed amounts of TMPyP (0.8544 g, 0.627 mmol) and copper acetate monohydrate (0.1251 g, 0.627 mmol) were dissolved in 20 mL of water. The metalloporphyrin formed immediately. The color of the solution was not very different from that of the aqueous solution of free base (422 nm in H_2O or in 1 mol dm^{-3} HCl) [6]. To this was added 0.2 g of γ-ZrP, and the mixture was shaken at 50 °C for 5 days. The solid was separated by centrifugation, washed with water, and air dried. The resultant crystallites (γ-ZrP/Cu-TMPyP) were subjected to XRD measurement.

2.6. INTERACTION OF TMPyP WITH γ-ZrP/Cu^{2+}

A preliminary experiment was carried out. γ-ZrP/Cu^{2+} was prepared as reported [3]. The solid was contacted with an equivalent molar aqueous solution of TMPyP at 50 °C for 1 day. XRD measurement was made on the resultant compound.

2.7. DIFFUSE REFLECTANCE SPECTRA OF γ-ZrP/TMPyP AND γ-ZrP/PMA-TMPyP

A color difference was observed for the two kinds of intercalates, γ-ZrP/TMPyP and γ-ZrP/PMA-TMPyP, and DR spectra were accordingly measured. For comparison, two aqueous solutions of TMPyP were prepared, one of which was acidified with hydrochloric acid. Absorption spectra were measured for both solutions, using a Shimadzu spectrophotometer. Further, mechanical mixtures of γ-ZrP and TMPyP solids with molar ratios of 10 : 1 and 20 : 1 were prepared and their DR spectra were measured. In some cases, the samples had been diluted with MgO powder in order to make peaks and valleys clearer than those in undiluted samples. Small fluctuations in the spectra over the wavelength range 300–350 nm are due to noise above the tolerance limit of the photomultiplier and can be ignored (Figures 1 and 3).

Table I. Uptake of TMPyP into γ-ZrP.

Sample No.	TMPyP taken/mg	Reaction period/day	Temperature °C	Interlayer distance Å	Composition of product
1	150	2	25	12.3	$Zr(PO_4)(H_2PO_4)TMPyP_{0.007} \cdot 1.2H_2O$
2	300	7	50	15.9	–
3	300	13	60	17.2	$Zr(PO_4)(H_2PO_4)TMPyP_{0.035} \cdot H_2O$

3. Results and Discussion

3.1. DIRECT INTERCALATION OF TMPyP INTO γ-ZrP

The reaction conditions and the resulting interlayer distances, as well as chemical composition, are given in Table I. If the interlayer distance of γ-ZrP, 12.3 Å, is simply subtracted from those of the intercalates obtained, the increment in interlayer distance is estimated to be 3.6–to 4.9 Å. The thickness of the porphyrin ring ranges from 4–6 Å, depending upon the angles between the porphyrin ring and the pyridine moiety. The observed results may indicate parallel orientation of porphyrin to the layer of γ-ZrP or slight tilting with an increase in loading, with the porphyrin and pyridine rings placed rather flat in the restricted interlayer space.

The area covered by TMPyP is more than 300 Å^2, whereas the free area associated with two hydroxyl groups is 33–36 Å^2 [7]. Uptake of 0.035 moles of TMPyP per formula weight of γ-ZrP is thus reasonable, if one takes into consideration the covering of some 20 active sites by a porphyrin molecule. The possibility of a bilayer assembly of porphyrins, as suggested for α-ZrP/p-H_2TAPP or α-ZrP/H_2TMPyP [2], can be ruled out because of the small increment in the interlayer distance, despite the fact that the charge density of γ-ZrP is higher than that of α-ZrP.

In clay minerals, Giannelis showed that Cu-TMPyP intercalated in hectorite interlayers lies parallel to the silicate layers, whereas the metalloporphyrin taken up in fluorohectorite interlayers is oriented at ~45° to the host layers [6]. The difference in orientation has been ascribed to the difference in the layer charge density of the two clay minerals.

In the present case, the charge density of the γ-ZrP layers is higher than that of smectite clays, provided that all hydroxyl groups are ionized. However, in intercalation of guest species like porphyrins, this is most probably not the case, since most of the active sites must remain unionized. Under these circumstances, TMPyP is likely to be oriented parallel to the host layer.

On the other hand, however, if the increment in interlayer distance is estimated by subtracting the interlayer distance of anhydrous γ-ZrP as an extreme case, the increment should be larger and a slight tilting of the porphyrin ring would result.

The crystallites (γ-ZrP/TMPyP) are green colored. DR spectra are shown in Figure 1, and indicate that the guest molecule is protonated, as suggested below. An example of XRD patterns of γ-ZrP/TMPyP (sample No. 3 in Table I) is shown

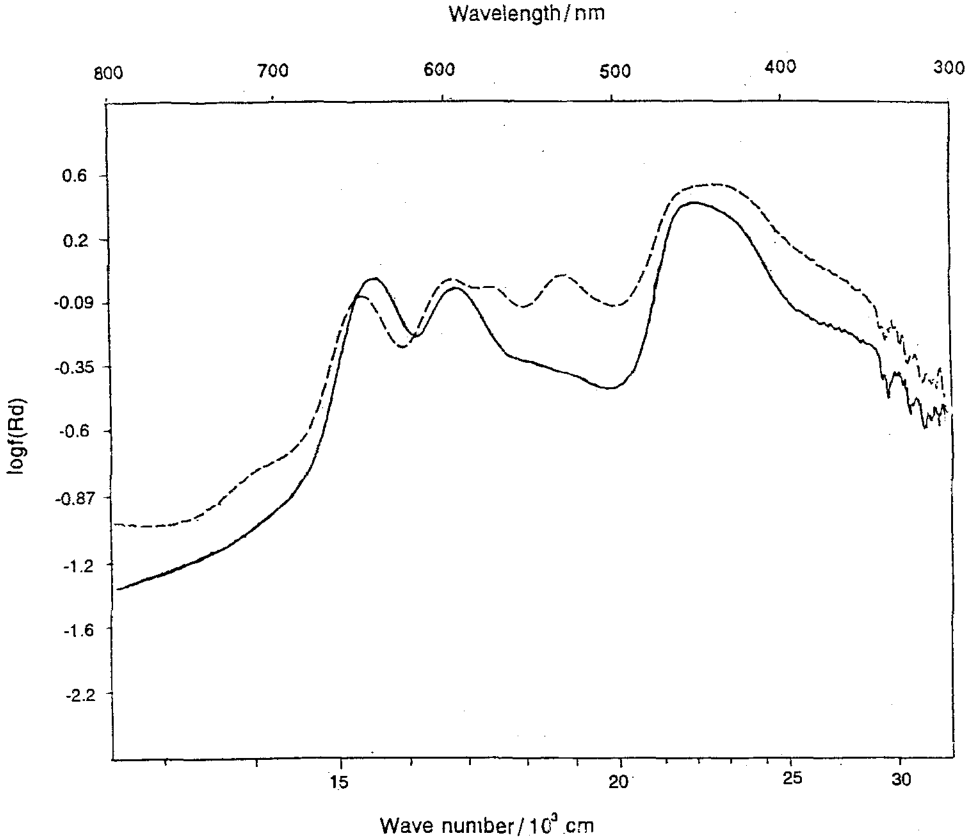

Figure 1. Diffuse reflectance spectra of (a) γ-ZrP/TMPyP (—), and (b) γ-ZrP/PMA-TMPyP (– – –). Each sample was diluted with MgO in order to improve the resolution.

in Figure 2. The predominant interlayer distance is 17.2 Å, but 20.5 and 12.3 Å (γ-ZrP) are also observed.

3.2. UPTAKE OF TMPyP INTO PMA-PRE-INTERCALATED γ-ZrP

Intercalation of PMA resulted in expansion of the interlayer distance of γ-ZrP from 12.3 to 18.6–18.9 Å. From elemental analysis, the chemical composition of one γ-ZrP/PMA intercalate was $Zr(PO_4)(H_2PO_4)(PMA)_{0.45} \cdot 1.1\ H_2O$. The net increment of the interlayer distance due to intercalation of PMA is difficult to estimate, because the number of water molecules decreased from 2 for the host to 1 for the intercalate. However, if we assume that the maximum increment is 18.9 minus 9.4, which is the interlayer distance of anhydrous γ-ZrP, 9.5 Å results. Comparing this value with the corresponding value of 15.4 Å for α-ZrP·2 PMA [2], the increment is much smaller. It is likely that, in the case of γ-ZrP, a monolayer of PMA molecules is formed, while a bilayer is formed in α-ZrP.

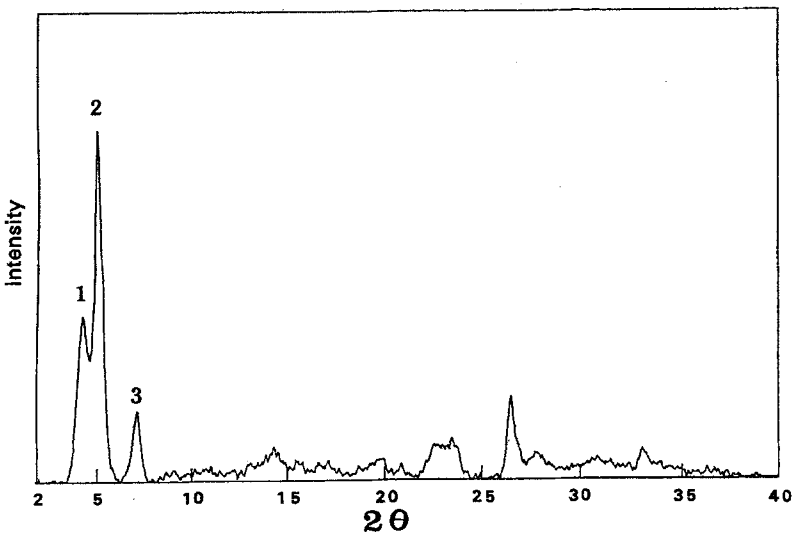

Figure 2. X-ray powder pattern of γ-ZrP/TMPyP (sample No. 3 in Table I). Peaks 1, 2 and 3 correspond to d values of 20.5, 17.2 and 12.3 Å, respectively.

The product after contacting with TMPyP was colored brown and the interlayer distance was 18.2–18.4 Å, which is slightly smaller than for the γ-ZrP/PMA intermediate, but the overall XRD pattern was very similar to the original intermediate. The C : N molar ratio of the product did not agree with either value for PMA or TMPyP. The result implies that the γ-ZrP/PMA intermediate failed to replace PMA with TMPyP between the interlayer region, but some TMPyP species were adsorbed on crystallite surfaces without protonation. Further evidence is shown in the DR spectrum of γ-ZrP/PMA-TMPyP (Figure 1). The spectrum is similar to those of the free base, with four Q bands between 500–700 nm.

3.3. COLOR CHANGE ACCORDING TO PROTONATION OF TMPyP

Figure 1 and Table II show DR spectra (Soret band) for the intercalates, γ-ZrP/PMA-TMPyP, γ-ZrP/TMPyP, mechanical mixtures of γ-ZrP and TMPyP with molar ratios of 10 : 1 and 20 : 1, respectively, and absorption spectra for an aqueous solution of TMPyP and an HCl-acidified TMPyP aqueous solution. It is known that the Soret band near 400 nm shifts to longer wavelength as a result of protonation of the porphyrin ring, and for a dication, the number of Q bands in the region of 450–700 nm decreases from four to two, accordingly [6].

With regard to the DR spectra of γ-ZrP/PMA-TMPyP and γ-ZrP/TMPyP, some data were obtained for samples diluted with MgO (Table III). In these cases, slight increases in λ_{max} values were observed on dilution. This trend might have occurred owing to adsorption of colored species on the MgO surface, as is often observed in DR spectra.

Table II. Diffuse reflectance and absorption spectra of intercalates and related substances.

Sample	Absorption maximum/nm	Color
γ-ZrP/TMPyP	432.3	Green
γ-ZrP/PMA-TMPyP	422.8	Brown
γ-ZrP + TMPyP (10 : 1)	443.7	Brown
γ-ZrP + TMPyP (20 : 1)	443.4	Brown
TMPyP aq.soln	421.0	Brown
TMPyP aq.soln + HCl	440.5	Green

Table III. Absorption maxima in diffuse reflectance spectra of γ-ZrP/PMA-TMPyP and γ-ZrP/TMPyP diluted with MgO.

γ-ZrP/PMA-TMPyP weight percent	Soret band /nm	Q-bands /nm			
100	423.3	527.4,	570.2,	646.1	
59.6	449.6	528.4,	592.6,	646.7	
30.1	439.0	528.0,	592.0,	647.7	
γ-ZrP/TMPyP weight percent					
100	433.0	592.6,	640.3		
59.2	443.2	592.0,	642.2		
29.3	450.2	592.0,	640.3		
(γ-ZrP + TMPyP) molar ratio					
10 : 1	445.3	520.8,	554.7,	591.5,	646.6
20 : 1	444.7	521.5,	592.8,	647.2	

The apparent color of γ-ZrP/TMPyP, as well as of an aqueous solution of TMPyP acidified with HCl, was green, while those of γ-ZrP/PMA-TMPyP, the mechanical mixtures of γ-ZrP and TMPyP and an aqueous solution of TMPyP were brown. This evidence suggests that in γ-ZrP/TMPyP, the porphyrin is mainly protonated, while in γ-ZrP/PMA–TMPyP and the mechanical mixture, it is not.

3.4. UPTAKE OF Cu^{2+} INTO γ-ZrP/TMPyP

Copper (II) ions were incorporated into the γ-ZrP/TMPyP intercalate up to the molar ratio of γ-ZrP : Cu^{2+} = 1 : 0.8. The change in pH of the supernatant was from 5.35 to 4.60. The reaction proceeded as follows.

$$\overline{\mathrm{H_2TMPyP}} + \mathrm{Cu}^{2+} \rightarrow \overline{\mathrm{CuTMPyP}} + 2\mathrm{H}^+$$

Table IV. Diffuse reflectance spectra of γ-ZrP/TMPyP-Cu diluted with MgO.

γ-ZrP/TMPyP-Cu weight percent	Soret band /nm	Q-bands /nm
100	409.6	554.6
77.6	414.1	555.8
39.8	428.8	556.2
9.96	429.8	556.2

Table IV gives the wavelengths of the Soret band and Q bands of γ-ZrP/TMPyP-Cu^{2+}. The rose color indicates formation of copper porphyrin (Figure 3) [6]. On the other hand, the interlayer distance of the product increased from 17.2 to 19.1 Å. Since the amount of Cu^{2+} ions taken up is much larger than the mole equivalent of TMPyP in the intercalate, excess of Cu^{2+} should be ion-exchanged with the hydroxyl group of γ-ZrP, also releasing hydrogen ions into solution.

$$\overline{\mathrm{Zr(PO_4)(H_2PO_4)}} + \mathrm{Cu^{2+}} \rightarrow \overline{\mathrm{Zr(PO_4)(CuPO_4)}} + 2\mathrm{H^+}$$

Carrado and Winans reported that transition-metal ion exchanged smectite clays reacted with free base porphyrins [6]. When Cu^{2+} or Co^{2+} ion-exchanged clays were used, corresponding metalloporphyrins were formed and released into solution.

Our preliminary experiment showed that, when Cu^{2+} ion-exchanged γ-ZrP was contacted with a TMPyP aqueous solution, no expansion of the interlayer spacing was observed. When TMPyP-intercalated γ-ZrP was contacted with an aqueous solution of copper acetate, the metalloporphyrin was formed in the interlayer space with expansion. Release of Cu-TMPyP was not observed.

The difference in behavior between γ-ZrP and clays toward metal ions and TMPyP may be due to the rigidity of γ-ZrP. The access of metal ions to TMPyP or release of metalloporphyrins must be more difficult in γ-ZrP than those in smectite minerals.

3.5. INTERCALATION OF Cu^{2+}-TMPyP INTO γ-ZrP

In this case, the interlayer distance was found to be 18.6 Å; the color was rose, and uptake proceeded rather easily. Thus, contact of the host with the guest solution for 5 days at 50 °C was effective, whereas 13 days at 60 °C was needed for the preparation of γ-ZrP/TMPyP. It is not immediately clear whether this is caused by geometrical accessibility of the guest species, because the interlayer distance is larger than that of γ-ZrP/TMPyP.

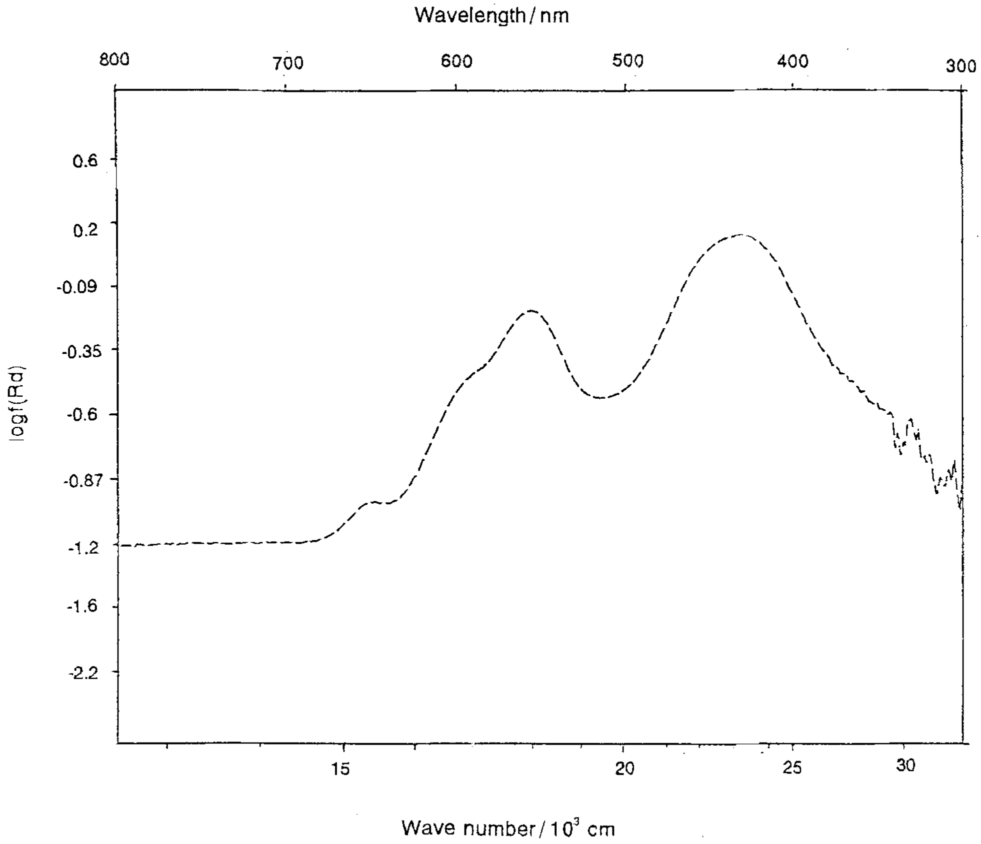

Figure 3. Diffuse reflectance spectrum of γ-ZrP/TMPyP-Cu^{2+}. The sample was diluted with MgO in order to improve the resolution.

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