Intercalation of Toluidines into α-Zirconium Hydrogenphosphate

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Abstract

Intercalates of *o*-, *m*-, and *p*-toluidine into α-Zr(HPO$_4$)$_2 \cdot$ H$_2$O were prepared and characterized by powder X-ray diffraction, thermogravimetric analysis and infrared spectroscopy. As follows from IR, toludine molecules are protonated in the interlayer space. Toluidine molecules are arranged in a bimolecular way in the intercalates containing more than 1.5 toluidine molecules per Zr atom. On the other hand, a monolayer of the toluidine molecules is supposed in the intercalates with less than one toluidine molecule per Zr atom.

Introduction

α-Zr(HPO$_4$)$_2 \cdot$ H$_2$O, (hereafter α-ZrP) is a layered compound, generated by the packing of two-dimensional macromolecular units that are weakly interacting with each other. Due to the presence of ionogenic P-OH groups on the surface of the layers, and to the easily accessible interlayer region, this compound is able to act as a host for cationic or molecular polar guest species. Host-guest chemistry of α-ZrP has been summarized in several reviews [1, 2] and books [3–5].

The intercalation of strong bases as alkylamines is driven by the acid-base interaction between the amino group and the P-OH group of the layer. The intercalation of aliphatic monoamines and diamines has been investigated by several workers [6–11]. The intercalation process usually occurs in well-defined steps indicating the presence of two or more solid phases and the final products contain one water molecule and two mono-amine or one diamine molecule per formula unit. The amine is usually protonated during the intercalation.

Less attention has been paid to the intercalation of aromatic amines. The intercalation of aniline [12, 13] and *p*-methoxyaniline [14] into α-ZrP and intercalation of *p*-phenylenediamine into α-titanium hydrogenphosphate [15] was reported. In the case of aniline and *p*-methoxyaniline, the intercalates containing two moles of the guest per one mole of zirconium with the basal spacings of 18.4 Å and 21.7 Å, respectively, were prepared. The guest molecules probably form a bilayer in the interlayer space, anchoring through a N–H–O hydrogen bonding to the host layers.

This paper reports on an intercalation of toluidines into α-zirconium hydrogenphosphate.

Experimental

Well-crystallized α-ZrP, of formula α-Zr(HPO$_4$)$_2 \cdot$H$_2$O, was obtained according to the method proposed by Alberti and Torracca [16]. A clear solution was prepared by dissolving 10.1 g of ZrOCl$_2 \cdot$8H$_2$O, 8 mL of hydro-fluoric acid (40% w/w) and 92 mL H$_3$PO$_4$ (85% w/w) in 160 mL of water. The solution was heated at 80 °C for 4 days, maintaining a constant volume by continuously adding water. α-ZrP precipitate was washed with de-ionized water and dried in air.

Intercalation of *o*-, *m*-, and *p*-toluidine into α-ZrP was studied. *p*-Toluidine was used as received, *o*- and *m*-toluidine were distilled before using. Pure intercalates were prepared as follows:

(a) Zr(HPO$_4$)$_2 \cdot$ 0.75(*o*-toluidine)·H$_2$O: α-ZrP (0.5 g, 1.66 mmol) was refluxed in 10 mL of *o*-toluidine (0.71 g, 6.64 mmol) aqueous solution for 6 h. Elem. anal. found (calcd.) C 16.8 (16.53) %; H 2.62 (2.84) %; N 2.61 (2.75) %.

(b) Zr(HPO$_4$)$_2 \cdot$1.5(*o*-toluidine)·H$_2$O: Zr(HPO$_4$)$_2 \cdot$0.75(*o*-toluidine)·H$_2$O intercalate was refluxed in 5 mL of pure *o*-toluidine for two hours. Elem. anal. found (calcd.) C 27.1 (27.30) %; H 3.52 (3.82) %; N 4.70 (4.55) %.

(c) Zr(HPO$_4$)$_2 \cdot$0.8(*m*-toluidine)·H$_2$O: α-ZrP (0.5 g, 1.66 mmol) was refluxed in 10 mL of *m*-toluidine (0.3 g, 2.8 mmol) aqueous solution for 8 h. Elem anal. C 17.2 (17.38) %; H 2.40 (2.92) %; N 3.11 (2.90) %.

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(d) $Zr(HPO_4)_2 \cdot 1.0(m\text{-toluidine}) \cdot 2H_2O$: α-ZrP (0.5 g, 1.66 mmol) was refluxed in 10 mL m-toluidine (0.71 g, 6.64 mmol) aqueous solution for 8 h. Elem. anal. found (calcd.) C 20.1 (19.72) %; H 3.09 (3.55) %; N 3.50 (3.29) %.

(e) $Zr(HPO_4)_2 \cdot 1.5(m\text{-toluidine}) \cdot H_2O$: α-ZrP (0.25 g 0.83 mmol), m-toluidine (0.55 g, 5 mmol), and 9 mL of H_2O was hydrothermally treated at 150 °C for 1 h. Elem. anal. found (calcd.) C 27.8 (27.30) %; H 3.91 (3.82) %; N 4.61 (4.55) %.

(f) $Zr(HPO_4)_2 \cdot 0.8(p\text{-toluidine}) \cdot H_2O$: α-ZrP (0.5 g, 1.66 mmol) was refluxed in 10 mL of p-toluidine (0.71 g, 6.64 mmol) aqueous solution for six hours. Elem. anal. found (calcd.) C 17.6 (17.38) %; H 3.12 (2.92) %; N 2.75 (2.90) %.

(g) $Zr(HPO_4)_2 \cdot 1.7(p\text{-toluidine}) \cdot 0.5H_2O$: α-ZrP (0.25 g, 0.83 mmol), p-toluidine (2.36 g, 22 mmol), and 9 mL of H_2O was hydrothermally treated at 130 °C for 1 h. Elem. anal. found (calcd.) C 29.8 (30.13) %; H 3.73 (3.89) %; N 5.39 (5.02) %.

The courses of the intercalation reactions were followed by acidobasic titrations. α-ZrP (0.25 g, 0.83 mmol) suspended in 50 mL H_2O was titrated with 0.166 M aqueous solution of the corresponding toluidine. In each step, 0.5 mL of the toluidine solution was added in 180-min intervals. The pH values were followed as a function of time.

X-ray powder diffraction (XRPD) patterns of the intercalates were obtained with an X-ray diffractometer (Krystaloflex-4, Germany) using Fe-filtered CoK_α radiation. The $CoK_{\alpha2}$ intensities were removed from the original data. Silicon ($a = 5.43055$ Å) was used as internal standard. Diffraction angles were measured from $2\theta = 2°$ to $2\theta = 40°$.

Compositions of the pure phases were calculated from thermogravimetry measurements and elemental analysis. The thermogravimetric analysis was done using a home-made apparatus constructed of a computer-controlled oven and a Sartorius BP210 S balance. The measurements were carried out in air between 30 and 950 °C at a heating rate of 3 °C min^{-1}. The weight of the gray rest obtained by heating to 950 °C was corrected for the carbon remained in the sample, which was determined by elemental analysis. The difference between the original weight of the sample and the corrected weight of the sample after heating is a weight of the organic substance, hydration water, and condensation water (water released by formation of pyrophosphate ZrP_2O_7). From the corrected weight of the heated sample, the amount of zirconium pyrophosphate was calculated which also corresponds to the amount of condensation water. The amount of hydration water corresponds to the weight loss observed to about 180 °C. The amount of the organic substance is calculated as a difference between the total weight loss and the amount of water. From the amount of the organic substance one can calculate content of N, C, and H in the sample and compare it with the results from elemental analysis. From these considerations the general formula of the intercalation compounds $Zr(HPO_4)_2 \cdot xNH_2C_6H_4CH_3 \cdot yH_2O$ was determined.

Infrared spectra of the solids were recorded on FT-IR spectrometer NEXUS (Nicolet, USA) in the range from 400 to 4000 cm^{-1} using a dry KBr powder containing 10% of the sample. The resulting reflectance spectra were converted to the Kubelka-Munk format. The spectra of the liquid guests were measured in a KBr cell.

Results and discussion

When the toluidine molecules enter between the host layers the concentration of the basic toluidine molecules in the solution decreases. This is accompanied by a decrease of pH, which can be observed. For the titration of the aqueous suspensions of α-ZrP, a 180-min time interval between additions of 0.5-mL doses of toluidine was chosen, so that the constant pH value was reached (see Figure 1). In the case of aliphatic amines [11, 17] and aminoalcohols [18], the reaction occurs in well-resolved steps and plateaus indicating the formation of the given intercalation compound with a characteristic value of the basal spacing and the guest content. In the case of toluidines, the reaction steps were not resolved probably due to their lower basicity.

The samples after titration contain a mixture of intercalates with different basal spacings. We tried to prepare pure individual intercalates by refluxing of α-ZrP in the corresponding toluidine aqueous solution or by the hydrothermal synthesis. In the case of o-toluidine and p-toluidine, the phases with lower guest content can be prepared very easily either by refluxing of the host with toluidine aqueous solution or by a
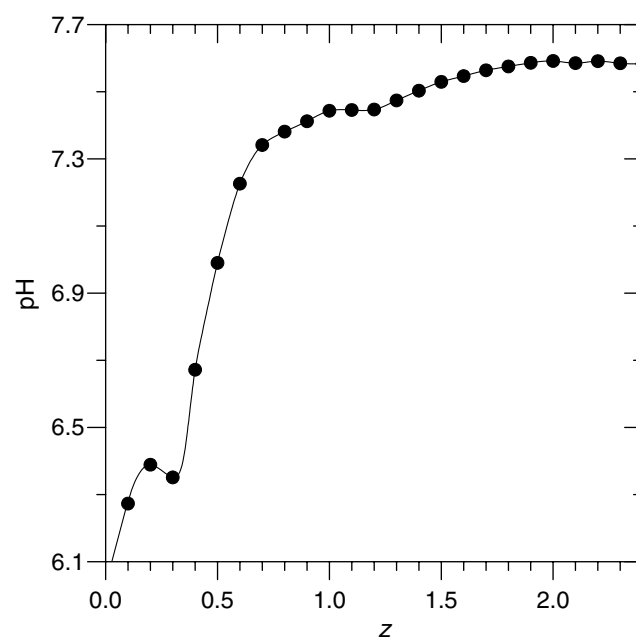

Figure 1. Potentiometric titration of α-ZrP/water suspension with p-toluidine solution ($z = p$-toluidine/Zr molar ratio).

hydrothermal synthesis using guest/host molar ratio 4:1. To prepare the phases with higher content of toluidine by the hydrothermal synthesis we varied guest/host molar ratio, reaction temperature and time. It was found that the guest/host molar ratio influences the products significantly but the changes of temperature (120–150°) and time (1–24 h) do not change the products at given guest/host ratio. If the hydrothermal syntheses were done with a high guest/host molar ratio (22:1) a pure intercalate with higher content of p-toluidine and a mixture of both o-toluidine intercalates were prepared. Pure phase with higher o-toluidine content was obtained by refluxing of $Zr(HPO_4)_2 \cdot 0.75(o$-toluidine)$\cdot H_2O$ intercalate in pure o-toluidine. On the other hand, the intercalate with higher content of m-toluidine forms easily either by refluxing or hydrothermally. The intercalate with lower content of m-toluidine was prepared by refluxing of ZrP with diluted m-toluidine solution (guest/host molar ratio 1.7:1). The procedures leading to the pure intercalates are given in detail in the experimental part.

All the intercalates prepared are white solids. The X-ray diffractograms of the intercalates prepared are given in Figure 2. The diffractograms contain two or three basal reflections. The calculated basal spacings are given in Table 1. The TG curves of both o-toluidine intercalates are given in Figure 3. The intercalated water is released up to 180 °C, o-toluidine is released at 180–250 °C. A weight decrease at 500–550 °C corresponds to the removal of condensation water and the formation of pyrophosphate ZrP_2O_7. A further slow decrease of the weight is caused by the combustion of the carbon formed by the decomposition of the toluidine. The final product of the heating is gray and contains some residual carbon. The decompositions of the m- and p-toluidine intercalates were similar, the corresponding total weight losses are given in Table 1.

The character of the interaction between the guest molecules and the host layers in the toluidine intercalates was studied using IR spectroscopy. As an example, the infrared spectrum of the $Zr(HPO_4)_2 \cdot 1.0(m$-toluidine)$\cdot 2H_2O$ intercalate together with spectra of the α-ZrP and pure m-toluidine are given in Figure 4. Comparing the positions of the vibration bands of the pure m-toluidine with these bands in the spectrum of the intercalate we observed some changes indicating that a proton transfer to intercalated toluidine occurred. In the N–H stretching region, the band at 2922 cm^{-1} and a very broad band at about 2640 cm^{-1} were observed. The $\delta_{as}(NH_3^+)$ and $\delta_s(NH_3^+)$ bands were found at 1560 and 1494 cm^{-1}, respectively. The C–N stretching vibration corresponding to protonated toluidine is observed at 1228 cm^{-1}. A very weak band at 1294 cm^{-1} could by assigned to the C–N vibration of unprotonated toluidine. The absence of the $v_{as}(NH_2)$ and $v_s(NH_2)$ bands, which are usually intensive, in the spectrum of the intercalate indicates that the proton transfer is almost complete and the amount of unprotonated toluidine in the interlayer space is very small.
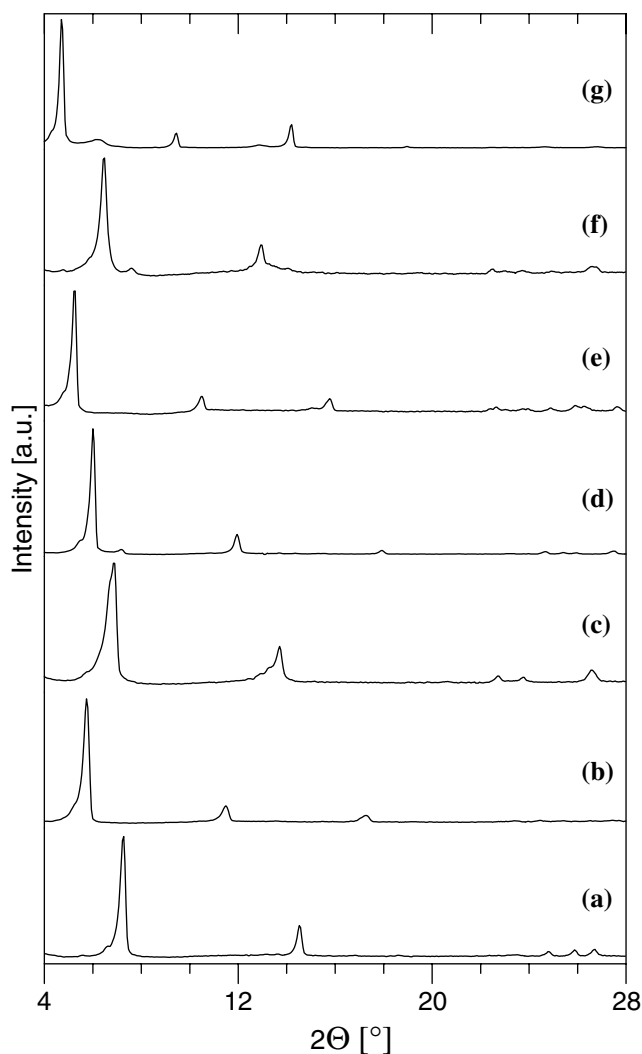

Figure 2. Powder X-ray diffractograms of the intercalates prepared: (a) $Zr(HPO_4)_2 \cdot 0.75(o$-toluidine)$\cdot H_2O$; (b) $Zr(HPO_4)_2 \cdot 1.5(o$-toluidine)$\cdot H_2O$; (c) $Zr(HPO_4)_2 \cdot 0.8(m$-toluidine)$\cdot H_2O$; (d) $Zr(HPO_4)_2 \cdot 1.0(m$-toluidine)$\cdot 2H_2O$; (e) $Zr(HPO_4)_2 \cdot 1.5(m$-toluidine)$\cdot H_2O$; (f) $Zr(HPO_4)_2 \cdot 0.8(p$-toluidine)$\cdot H_2O$; (g) $Zr(HPO_4)_2 \cdot 1.7(p$-toluidine)$\cdot 0.5H_2O$.

Table 1. The basal spacings and TGA results of the intercalates prepared

	Formula	Basal spacing [Å]	Total weight loss [%]	
			Found	Calculated
a	$Zr(HPO_4)_2 \cdot 0.75(o$-toluidine)$\cdot H_2O$	14.16	30.8	30.5
b	$Zr(HPO_4)_2 \cdot 1.5(o$-toluidine)$\cdot H_2O$	17.88	43.0	42.6
c	$Zr(HPO_4)_2 \cdot 0.8(m$-toluidine)$\cdot H_2O$	15.03	26.0*	31.5
d	$Zr(HPO_4)_2 \cdot 1.0(m$-toluidine)$\cdot 2H_2O$	17.32	38.0	37.8
e	$Zr(HPO_4)_2 \cdot 1.5(m$-toluidine)$\cdot H_2O$	19.65	42.0	42.6
f	$Zr(HPO_4)_2 \cdot 0.8(p$-toluidine)$\cdot H_2O$	15.88	27.5*	31.5
g	$Zr(HPO_4)_2 \cdot 1.7(p$-toluidine)$\cdot 0.5H_2O$	21.72	42.5	44.1

*Sample after TG analysis contained about 4% carbon.

The spectra of the host and the intercalate exhibit many common features. The positions of the $v_1(PO_4)$ and $v_3(PO_4)$ bands in the spectrum of the intercalate
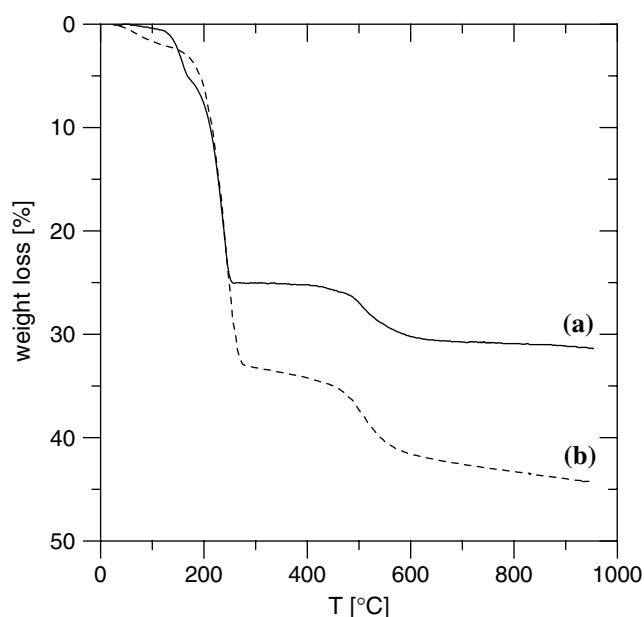
Figure 3. TG curves of the Zr(HPO$_4$)$_2$·0.75(*o*-toluidine)·H$_2$O (a) and Zr(HPO$_4$)$_2$·1.5(*o*-toluidine)·H$_2$O (b) intercalates.

Figure 4. IR spectra of the Zr(HPO$_4$)$_2$·0.8(*m*-toluidine)·H$_2$O intercalate, α-ZrP, and pure *m*-toluidine.

bands observed in the spectrum of the host at 3593 and 3510 cm^{-1} and attributed to the (P–)O–H stretching modes remain at the same position but their intensities are markedly lower in the spectrum of the intercalate. The intensities of these bands decrease with increasing amount of toluidine intercalated. The observed changes in the positions and intensities of the bands corresponding to the P–O–H vibration are probably caused by the differences in the hydrogen bonding scheme in the host and in the intercalate.

The X-ray diffraction structure analysis is usually difficult in the case of the intercalates. Their diffractograms are often affected by many phenomena like disorder in the arrangement of the guest molecules in the interlayer space and disorder in the stacking of the layers. As a result of this disorder, it is almost impossible to prepare a single crystal suitable for the diffraction analysis. The powder diffraction patterns are in addition influenced by a strong preferred orientation. Therefore the arrangement of the guest molecules in the interlayer space is usually suggested on the basis of the steric demands of the guest molecules, host layer thickness, and the experimentally found basal spacing and composition of the intercalate. In the case of α-ZrP, the layer thickness is 6.3 Å and the free area associated with each P-OH group is 24 Å^2 [19].

The proposed arrangement of the *p*-toluidine molecules in the Zr(HPO$_4$)$_2$·1.7(*p*-toluidine)·0.5H$_2$O intercalate is depicted in Figure 5a. The *p*-toluidine molecules form bilayers with their N–C bond almost perpendicular to the host layer plane. The basal spacing of this intercalate is about 3.3 Å higher than that of the aniline intercalate [13], which is in agreement with the difference in the van der Waals length of both molecules (8.0 Å for aniline, 9.3 Å for *p*-toluidine). The cross section of the *p*-toluidine molecule (22 Å^2) is lower than the free area of α-ZrP so that the ideal composition of the intercalate should be Zr(HPO$_4$)$_2$·2(*p*-toluidine)·yH$_2$O. The lower *p*-toluidine content in the intercalate prepared could be ascribed to a presence of a small amount of the phase with lower basal spacing in our product (see Figure 2g).

The van der Waals length of the *o*- and *m*-toluidine molecules is practically the same as that of the aniline molecules. The cross section of these molecules is higher (about 28 Å^2) than in the case of *p*-toluidine due to the presence of the methyl group in the *o*- or *m*-position. As the cross section is higher than the free area of α-ZrP, the toluidine content could be smaller than 2 toluidine molecules per Zr atom, which is in agreement with our experimental results. As follows from the basal spacings measured (17.88 Å for the *o*-toluidine intercalate, 19.65 Å for the *m*-toluidine intercalate), the toluidine molecules form a bilayer in the interlayer space similarly as the *p*-toluidine molecules. The basal spacing of the *o*-toluidine intercalate is slightly smaller than that of the aniline intercalate, so we presumed that the *o*-toluidine molecules are slightly interdigitated. In the case of the *m*-toluidine, this interdigitation is not possible due to the methyl group, the *m*-position, and the basal spacing of
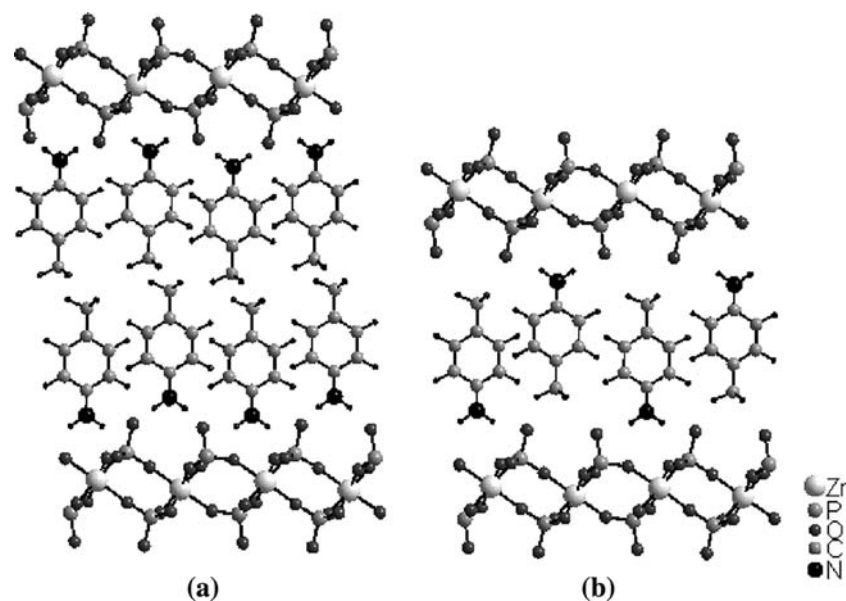
(1064, 1032, 1103, and 1150(sh) cm^{-1}) only slightly differs from the positions of those bands in α-ZrP (1064, 1026, 1116, and 1149(sh) cm^{-1}). Badly resolved doublet corresponding to the δ(POH) out-of-plane vibration is shifted to the higher frequency in the spectrum of the intercalate (about 960 cm^{-1} for α-ZrP, about 990 cm^{-1} for the intercalate). The band corresponding to the δ(POH) in-plane vibration observed at 1250 cm^{-1} in the spectrum of the host is probably overlapped by the band at 1228 cm^{-1} which could be assigned to the C–N stretching vibration of protonated toluidine. Two sharp

Figure 5. Proposed arrangement of the *p*-toluidine molecules in the $Zr(HPO_4)_2 \cdot 0.8(p\text{-toluidine}) \cdot H_2O$ (a) and $Zr(HPO_4)_2 \cdot 1.7(p\text{-toluidine}) \cdot 0.5H_2O$ (b) intercalates.

this intercalate is higher than that of the aniline intercalate.

The proposed arrangement of the *p*-toluidine molecules in the $Zr(HPO_4)_2 \cdot 0.8(p\text{-toluidine}) \cdot H_2O$ intercalate is depicted in Figure 5b. Comparing the van der Waals length of the *p*-toluidine molecule with the increase in the galery height (15.88 Å–6.3 Å = 9.58 Å) we can suppose that the toluidine molecules form a monolayer whereby the amino groups are oriented alternately to the layer above and below. The *o*- and *m*-toluidine molecules are arranged in the similar way in the intercalates containing 0.75 or 0.8 toluidine molecules per Zr atom.

Acknowledgement

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