

Layered Zincophosphate Materials Prepared from a Molecular Zinc Di(*tert*-butyl)phosphate Complex in Organic Solvents

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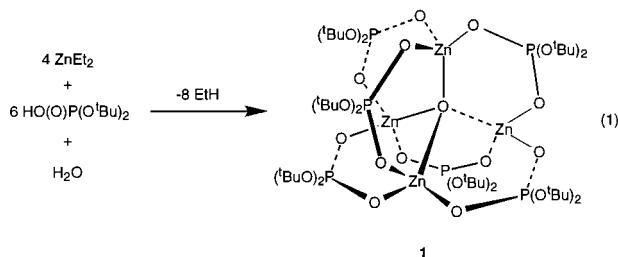
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Layered zincophosphate materials were prepared from the molecular precursor $Zn_4(\mu_4-O)[O_2P(O^tBu)_2]_6$ (**1**) via thermolysis (180–215 °C) in anhydrous organic solvents in the presence of long-chain primary amines. Through variation of the amine concentration, two series of materials were obtained with the stoichiometries $Zn_2(HPO_4)_3(H_3NC_nH_{2n+1})_2$ and $Zn_2(HPO_4)_3(H_3NC_nH_{2n+1})_2(H_2NC_nH_{2n+1})$ ($n = 8–16$). These materials possess an unusual Zn/P ratio of 2:3 which is uncommon for layered zincophosphate materials prepared in aqueous media.

Introduction

We have been exploring use of $Zn_4(\mu_4-O)[O_2P(O^tBu)_2]_6$ (**1**), prepared by the reaction of $ZnEt_2$ and $HO(O)P(O^tBu)_2$ (eq 1), as a “single-source molecular precursor” to zinc phosphate materials. Solutions of **1** react with 1,6-hexanediamine at room temperature to form a layered coordination network with the formula $\{Zn[O_2P(O^tBu)_2]_2[H_2N(CH_2)_6NH_2]\}_n$, and under acidic conditions, **1** is converted to the one-dimensional polymer $\{Zn[O_2P(O^tBu)_2]_2\}_n$.¹ When heated above 134 °C, **1** cleanly loses



its “hydrocarbon shell” (as isobutene) to produce zinc phosphate materials. As an extension of our earlier work, we have been interested in examining **1** as a single-source precursor to mesostructured materials. One approach, described here, involves the use of organic surfactants as structure-directing agents for the assembly of inorganic networks. Given the hydrolytic instability of **1**, we have primarily employed nonaqueous solvents for these conversions. In related work, it has been shown that mesostructured materials may be derived from sol-gel processes in organic solvent systems.²

Since the original synthesis of hexagonally ordered mesoporous silicates using micelle-assisted templating,³ many variants

of this approach have been explored. A variety of charged⁴ and neutral surfactants such as primary amines^{2,5,6} and poly-(ethylene oxide) oligomers⁷ have been employed as effective templates for the synthesis of mesostructured materials. Such methods have targeted not only silica-based materials but also mesoporous transition-metal oxides,^{2,8} phosphates,^{5,9} and sulfates.^{9a} Recently, Stucky et al. reported the synthesis of lamellar zinc phosphates from aqueous solutions containing ammonium bromide surfactants.¹⁰

Results and Discussion

The general procedure for preparing layered zinc phosphate mesophases involved charging an ampule with $Zn_4(\mu_4-O)[O_2P(O^tBu)_2]_6$ (**1**), 2–10 equiv of a primary amine (e.g., 1-hexadecylamine), and a solvent such as toluene, 2-propanol, or ethanol. The ampule was sealed under an inert atmosphere and then

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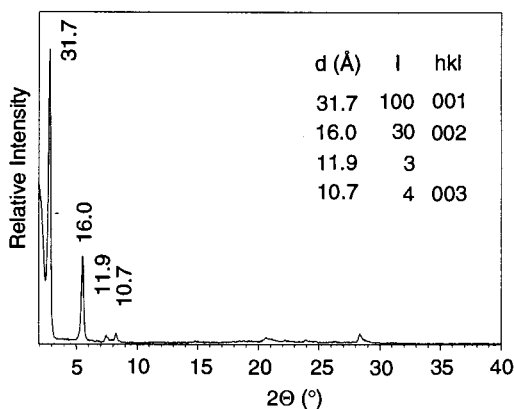


Figure 1. XRD pattern of **2** having a layer spacing of 31.7 Å.

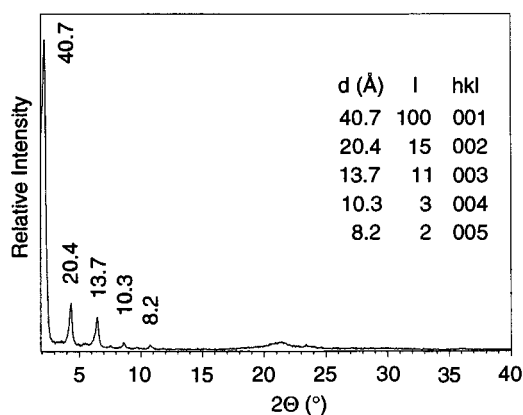


Figure 2. XRD pattern of **3** having a layer spacing of 40.7 Å.

heated in an oven for ca. 12 h, resulting in formation of a gel. The solid was isolated by filtration and then washed with toluene, ethanol, and water.

A layered material (**2**) with an interlayer spacing of 31.7 Å [from X-ray diffraction (XRD), Figure 1] was formed when the reaction was carried out in 2-propanol with 4 equiv of *n*-hexadecylamine at 185 °C. With toluene as the solvent, this reaction afforded a layered material with poorer crystallinity, as judged by the resolution of high-index peaks in the XRD spectrum at 2θ values of 32.2, 15.9, and 10.6°. Lowering the amount of amine to 2 equiv of hexadecylamine gave only amorphous powders from toluene, and in 2-propanol this reaction gave a mixture of Zn₃(PO₄)₂ and some of the layered material mentioned above (*d* spacing: 32.2 Å, by XRD). With 6 equiv of 1-hexadecylamine, a similar material is obtained from 2-propanol (*d* spacing: 31.8 Å), but in toluene, a material with a 41.0-Å layer spacing was produced. The latter material appears to be associated with a greater incorporation of amine into the layered structure, because the reaction of **1** with 8 equiv of 1-hexadecylamine in toluene at 215 °C produced a material (**3**) with a layer spacing of 40.7 Å (by XRD, Figure 2). With 10 equiv of 1-hexadecylamine, a material with a 42.1-Å layer spacing was produced in toluene. Precipitation of these layered materials leaves a basic supernatant (pH 8–10). The solid products were not contaminated with excess amine or the ammonium phosphate (by XRD), which was independently prepared from a 1:1 mixture of H₃PO₄ and 1-hexadecylamine.

These results indicate that two types of layered phases are formed, depending on the zinc/amine ratio, with layer spacings of ca. 41 and 31 Å (Table 1). Changes in solvent or temperature, for reactions involving 4 or 8 equiv of amine, produce only small variations in the layer spacing. However, no systematic trends correlating reaction conditions with the

Table 1. Summary of Layered Phases Derived from **1**^a

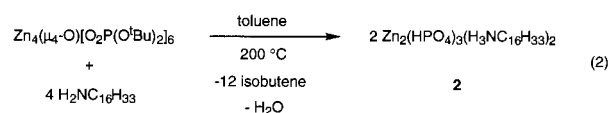
amine	equiv amine	solvent	reaction temperature (°C)	<i>d</i> (001) (Å)
H ₂ NC ₁₆ H ₃₃	2	toluene	200	
H ₂ NC ₁₆ H ₃₃	2	2-propanol	180	32.4 ^b
H ₂ NC ₁₆ H ₃₃	4	toluene	200	32.2
H ₂ NC ₁₆ H ₃₃	4 ^c	2-propanol	185	31.7
H ₂ NC ₁₆ H ₃₃	6	toluene	200	41.0
H ₂ NC ₁₆ H ₃₃	6	2-propanol	200	31.8
H ₂ NC ₁₆ H ₃₃	8 ^d	toluene	215	40.7
H ₂ NC ₁₆ H ₃₃	8	2-propanol	180	41.7
H ₂ NC ₁₆ H ₃₃	10	toluene	200	42.1
H ₂ NC ₁₆ H ₃₃	10	2-propanol	200	41.5
H ₂ NC ₈ H ₁₇	4	2-propanol	200	22.1
H ₂ NC ₈ H ₁₇	8	2-propanol	200	26.2
H ₂ NC ₁₀ H ₂₁	4	2-propanol	200	23.8
H ₂ NC ₁₀ H ₂₁	8	2-propanol	200	30.4
H ₂ NC ₁₂ H ₂₅	4	2-propanol	200	27.6
H ₂ NC ₁₂ H ₂₅	8	2-propanol	200	33.9
H ₂ NC ₁₄ H ₂₉	4	2-propanol	200	29.9
H ₂ NC ₁₄ H ₂₉	8	2-propanol	200	37.7

^a Obtained by varying the number of carbon atoms in the amine alkyl chain, amine concentration, and solvent. ^b Zn₃(PO₄)₂ also present. ^c This procedure gave **2**. ^d This procedure gave **3**.

resulting layer spacings of the product were observed. These small variations in the *d* spacings are within experimental error and are most likely due to systematic errors inherent to low-angle reflections.

The XRD pattern of **2** (prepared with 4 equiv of 1-hexadecylamine) revealed three peaks that could be indexed as 001 reflections in a crystal system characterized by an orthogonal *c* direction (Figure 1). The absence of other peaks indicates that there is little registry between the layers of this material. The broad low-intensity peaks between 20 and 30° 2θ are characteristic of diffraction from the packed alkyl chains within the layers.^{4b} The XRD pattern of **3** contains peaks that can be indexed as the first five 001 reflections (Figure 2), indicating the presence of longer-range order in the layers of **3** vs **2**. Again, the absence of other reflections indicates that there is little registry between the layers. The transmission electron micrograph of **3** (Figure 3) clearly illustrates the layered structure of this material, and the layer spacing measured from this photograph (39 Å) is consistent with the XRD data.

Analytically pure samples of these mesophased materials are difficult to obtain, given the inherent difficulty in purifying insoluble materials. However, elemental analyses and spectroscopic data are most consistent with a stoichiometry of Zn₂(HPO₄)₃(H₃NC₁₆H₃₃)₂ for **2**. Such a material incorporates all of the zinc, phosphorus, and amine supplied to the reaction (eq 2). The IR spectrum for **2** contains a broad shoulder at 3200



cm⁻¹, consistent with the presence of ammonium ions. Thermal gravimetric analysis (TGA) of **2** revealed a gradual weight loss between 200 and 400 °C (under nitrogen) and a ceramic yield at 800 °C of 48.8%. This value is somewhat higher than the theoretical yield for (ZnO)₂(P₂O₅)_{1.5} (41.6%). The dark gray color of the thermolyzed material suggests that it contains significant amounts of carbon because of incomplete combustion of the organic portion of the material.

The reaction of **1** with more than 4 equiv of amine appears to result in the incorporation of neutral amines into the interlayer spaces of **2**, without modification of the inorganic portion of

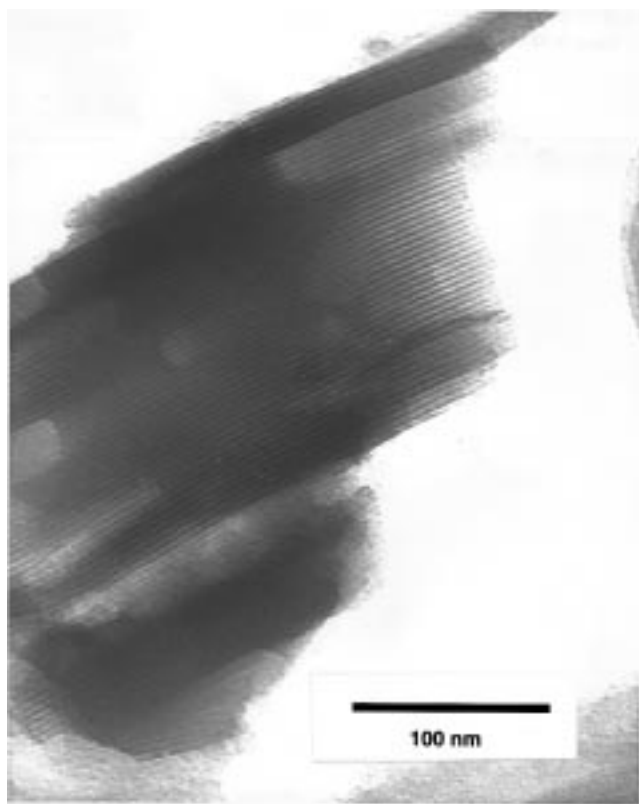


Figure 3. TEM photograph of **3**.

the structure. Thus, the combustion analysis of **3** is consistent with addition of 1 equiv of hexadecylamine/formula unit of **2** and the formula $\text{Zn}_2(\text{HPO}_4)_3(\text{H}_3\text{NC}_{16}\text{H}_{33})_2(\text{H}_2\text{NC}_{16}\text{H}_{33})$. TGA of **3** revealed a gradual weight loss between 200 and 400 °C and a ceramic yield at 800 °C of 35.0%, which is close to the calculated ceramic yield of 32.8% for $(\text{ZnO})_2(\text{P}_2\text{O}_5)_{1.5}$. The thermolysis residue from **3** is also gray. The IR spectrum of **3** contains a broad peak at 3200 cm^{-1} assigned to ammonium (RNH_3^+) ions and a peak at 3400 cm^{-1} attributed to the presence of an amine.¹¹ The neutral amine is possibly coordinated to zinc atoms in the inorganic layer, rather than simply clathrated between the alkylammonium ions, because **3** forms from reaction mixtures with a range of amine concentrations. If the amines were occluded within the organic layers without having specific interactions with the inorganic layer, then the layers could be swollen to arbitrary layer spacings (which is not observed). In addition, once formed, **2** and **3** do not swell after exposure to a variety of solvents. Structural studies on lamellar zinc phosphonates intercalated with primary amines have shown that the amines coordinate to the zinc atoms of the inorganic layers.¹² Similarly, the neutral amines in **3** may coordinate to the zinc atom, thus leading to a well-defined stoichiometry.

Recently, the structure of a layered zinc phosphate with the stoichiometry $[\text{Zn}_2\text{P}_3\text{O}_9(\text{OH})_3]^{2-}[\text{NH}_3(\text{CH}_2)_4\text{NH}_3]^{2+}$ was reported.¹³ This material, which also has a Zn/P ratio of 2:3, was synthesized from phosphoric acid and a 1,4-diaminobutane complex of zinc. The latter coordination complex is, therefore, the source of both the zinc ions and the "template" molecules. We believe that in an analogous manner amine–zincophosphate

complexes are intermediates in the formations of **2** and **3**. Evidence for the existence of such complexes comes from isolation of a coordination network with the formula $\{\text{Zn}[\text{O}_2\text{P}(\text{O}^i\text{Bu})_2][\text{H}_2\text{N}(\text{CH}_2)_6\text{NH}_2]\}_n$, prepared from a mixture of **1** and 1,6-hexanediamine in a toluene/dichloromethane solution.¹

The 2:3 ratio of zinc to phosphorus in the above materials contrasts with that associated with well-known zinc phosphonate compounds of the type $\text{Zn}(\text{O}_3\text{PR})(\text{L})$ ($\text{L} = \text{H}_2\text{O}, \text{R}'\text{NH}_2$), which are also layered.^{12,14} Other surfactant-templated lamellar zinc phosphates have been obtained by hydrothermal methods.¹⁰ In the latter approach, variations in the pH and the composition of the reaction mixture produced several layered materials with various d spacings. One of these phases was determined to have a Zn/P ratio of 1:1, and compositions for the rest were not reported.¹⁰ Three-dimensional zincophosphate materials with a large variety of Zn to P ratios, including 2:3,^{15g} have also been prepared.¹⁵

Studies on the intercalation of primary amines into the layers of zinc phosphonates have appeared.¹² Mallouk and Cao found that for certain sets of n -alkylamines there is a linear relationship between the layer spacing of the intercalated zinc phosphonate and the number of carbon atoms in the amine alkyl chain.^{12a} The orientation of the alkyl chains could be inferred from the slope of the linear relation between the interlayer distance and the number of carbon atoms in the alkyl chain. With a slope greater than $1.27\text{ \AA}/\text{CH}_2$ unit (for an all-trans linear alkyl chain), the amine tails were interpreted as being arranged in a double-layer fashion. In this case, the tilt angle of the chains with respect to the inorganic layer (Θ) may be calculated from the expression $\sin^{-1}(\text{slope}/2 \times 1.27)$ (see Figure 4a). If the slope is less than $1.27\text{ \AA}/\text{CH}_2$ unit, the alkyl chains may be interdigitated, with a tilt angle for the alkyl chains (Θ) of $\sin^{-1}(\text{slope}/1.27)$ (Figure 4b). Alternatively, such values may imply a double-layer arrangement with a very small tilt angle (Θ) for the alkyl chains.

Two series of lamellar zinc phosphate phases were prepared, based on 4 and 8 equiv of n -alkylamines, with the alkyl chains ranging in length from octyl to hexadecyl. The syntheses were carried out in 2-propanol, by heating to 200 °C for 12 h. The measured interlayer spacings for these materials are plotted against the number of carbon atoms in the n -alkyl chain of the amine in Figure 5. The slope of 1.84 for materials prepared with 8 equiv of amine is much larger than $1.27\text{ \AA}/\text{CH}_2$, indicating that the alkyl chains are arranged in a double-layer fashion with a tilt angle of 46° (Figure 4a). A slope of 1.17 was obtained for materials prepared with 4 equiv of amine, indicating that the alkyl chains in these samples are interdigitated with a tilt angle of 67° (Figure 4b). However for the latter samples, we cannot rule out the possibility that the alkyl chains are arranged in a double-layer fashion, with a very small tilt angle of 27° .

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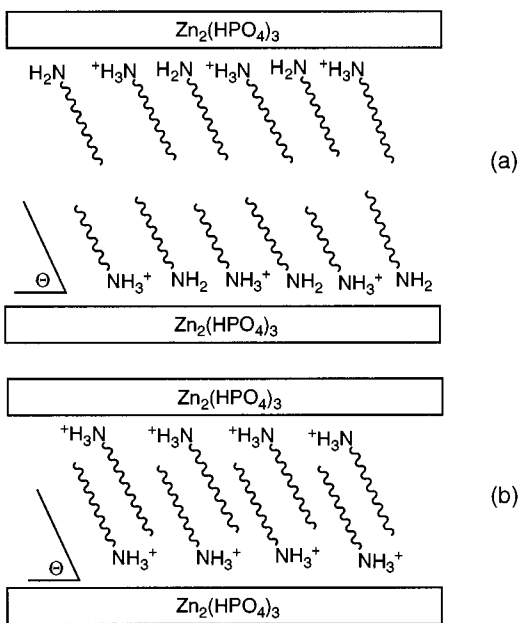


Figure 4. Schematic showing (a) a double-layer arrangement of the amine alkyl chains possibly present in the materials made with 8 equiv of amine and (b) an interdigitated arrangement of the amine chains possibly present in the materials made with 4 equiv of amine. The tilt angle of the amine chains (Θ) is also indicated.

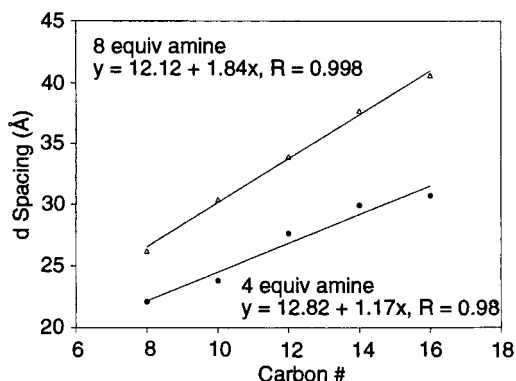


Figure 5. Plot of the interlayer spacing vs the carbon number in the n -alkylamine chain for the two series of materials made with 4 (filled circles) and 8 (open triangles) equiv of amine.

Conclusion

Complex **1** has been investigated as a single-source precursor for the synthesis of zincophosphate mesophases in organic solvents. Under these conditions, the formation of lamellar phases is to be expected given the high surfactant content. In addition, in the absence of a polar solvent, it is difficult to access specific surfactant mesophases by tuning the solvent/surfactant ratio. Elemental analyses of the mesophases suggest that the Zn/P ratio of **1** is retained in the layered materials. Thus, this

nonaqueous synthesis has produced lamellar zincophosphate mesophases with an unusual Zn/P ratio which has been observed in only one other lamellar zincophosphate material,¹³ obtained via aqueous routes.

Experimental Section

General. All manipulations were performed under a nitrogen atmosphere using standard Schlenk techniques or a Vacuum Atmospheres drybox using dry, oxygen-free solvents. Infrared spectra were collected as Nujol mulls on a Mattson Galaxy 3000 spectrometer, using CsI windows. Electron microscopy was performed on a JEOL 100CX, and thermal analyses were obtained with a DuPont model 2000 thermal analysis system. Powder X-ray diffraction patterns were obtained with a Siemens D5000 spectrometer with a scintillation counter operating in a $\Theta-2\Theta$ geometry. Data were collected with a step size of 0.05° using Cu $K\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$). The synthesis of $\text{Zn}_4(\mu_4\text{-O})[\text{O}_2\text{P}(\text{O}^i\text{Bu})_2]_6$ (**1**) was reported previously.¹

Layered Material with 31.7-Å Layer Spacing (2). A 30-mL heavy-walled glass ampule was charged with **1** (0.10 g, 0.065 mmol), 1-hexadecylamine (0.064 g, 0.27 mmol), and 2-propanol (1.0 mL). The ampule was sealed under nitrogen and placed in an oven preheated to 185°C . Over the course of several hours, a white gel formed from a clear reaction solution. The reaction mixture was heated for a total of 12 h. The solid product was collected on a filter, washed with toluene, ethanol, and water, and then allowed to air-dry for 12 h. Anal. Calcd for $\text{C}_{32}\text{H}_{75}\text{N}_2\text{O}_{12}\text{P}_3\text{Zn}_2$: C, 42.53; H, 8.37; N, 3.10; P, 10.28; Zn, 14.47. Found: C, 42.46; H, 8.43; N, 2.48; P, 10.26; Zn, 19.74. IR (KBr pellet, cm^{-1}): 3200 (br sh), 2922 (s), 2852 (m), 1637 (m), 1543 (m), 1470 (m), 1396 (w), 1153 (s), 1138 (w sh), 1063 (s), 1028 (s), 976 (m), 793 (w), 721 (s), 627 (m), 609 (w), 567 (w), 476 (w).

Layered Material with 40.7-Å Layer Spacing (3). A 30 mL heavy-walled glass ampule was charged with **1** (0.10 g, 0.065 mmol), 1-hexadecylamine (0.128 g, 0.53 mmol), and toluene (0.6 mL). The ampule was sealed under nitrogen and placed in an oven preheated to 215°C . Over the course of several hours, a white gel formed from a clear reaction solution. The reaction mixture was heated for a total of 12 h. The solid product was collected on a filter, washed with toluene, ethanol, and water, and then allowed to air-dry for 12 h. Anal. Calcd for $\text{C}_{48}\text{H}_{110}\text{N}_3\text{O}_{12}\text{P}_3\text{Zn}_2$: C, 50.35; H, 9.68; N, 3.67; P, 8.11; Zn, 11.42. Found: C, 48.28; H, 9.65; N, 3.53; P, 7.64; Zn, 11.91. IR (Nujol, cm^{-1}): 3200 (br sh), 1636 (m), 1628 (m sh), 1578 (m), 1554 (w), 1160 (s), 1117 (s), 1091 (m), 1019 (s), 986 (m), 935 (m), 886 (m), 722 (m), 631 (m), 591 (w), 556 (m).

General Synthesis of Layered Materials with Intercalated Amines. For these syntheses, a 30-mL heavy-walled glass ampule was charged with **1** (0.05 g, 0.033 mmol), 4 or 8 equiv of the appropriate amine, and 2-propanol (0.5 mL). The ampule was sealed under nitrogen and placed in an oven preheated to 200°C . The reaction mixture was heated for a total of 12 h. The solid product was collected on a filter, washed with toluene, ethanol, and water, and then allowed to air-dry.

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