

Synthesis and Characterization of a New Layered Lithium Zinc Phosphate Hydrate

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A new layered lithium zinc phosphate hydrate, $\text{Li}_2\text{Zn}(\text{HPO}_4)_2 \cdot 0.66\text{H}_2\text{O}$, isostructural with $\text{Na}_2\text{Zn}(\text{HPO}_4)_2 \cdot 4\text{H}_2\text{O}$ was prepared by the direct ambient pressure and temperature reaction between zinc 2,4-pentanedionate, phosphoric acid, and lithium hydroxide. The as-prepared sample is monoclinic ($a = 8.896(8) \text{ \AA}$, $b = 13.092(5) \text{ \AA}$, $c = 10.882(9) \text{ \AA}$, and $\beta = 115.760(6)^\circ$). The prepared solid undergoes three thermal transformations when it is heated from 110 to 600°C. The first two transformations are due to the release of intercalated water molecules and the third one is due to the $\text{HPO}_4^{2-} \rightarrow \text{P}_2\text{O}_7^{4-}$ transition. © 2001 Academic Press

Key Words: layered phosphate; zincophosphate; ambient conditions; intercalated water molecules.

INTRODUCTION

Layered acid phosphates are of continuing academic and industrial interest because of their extensive use as heterogeneous catalysts (1–3). Some of them can undergo ion exchange and reversible hydration in the same way as zeolites. Recently, we developed a new room-temperature synthetic route for the preparation of layered acid phosphates of magnesium. The interlayer species were water (4, 5), ethanol, and ethylene glycol (6). The water intercalated magnesium phosphate can undergo reversible dehydration–rehydration provided it is not heated beyond 200°C. There is a growing interest in the preparation of new non-aluminosilicate framework materials with structures that include very large pores. Indeed, some of the zinc phosphate structures exhibit channels with diameters exceeding 14 Å (7–9).

Recently, Harrison and co-workers (10) prepared a new layered two-dimensional zincophosphate material, $\text{Na}_2\text{Zn}(\text{HPO}_4)_2 \cdot 4\text{H}_2\text{O}$, containing a network of layers of bifurcated tetrahedral 12-rings connected by sodium cations and H-bonds. Here, we report the preparation of a new layered lithium zinc phosphate isostructural with

$\text{Na}_2\text{Zn}(\text{HPO}_4)_2 \cdot 4\text{H}_2\text{O}$ using a simple ambient conditions synthetic method. The prepared solid was characterized by X-ray powder diffraction and IR spectroscopy. The thermal transformations were investigated by thermogravimetric measurements (TG), differential scanning calorimetry (DSC), and X-ray powder diffraction.

EXPERIMENTAL

The title compound was prepared at room temperature by mixing in distilled water zinc 2,4-pentanedionate $\text{Zn}(\text{C}_5\text{H}_7\text{O}_2)_2 \cdot \text{H}_2\text{O}$ (Johnson Matthey Electronics) with phosphoric acid (99.999%, 85 wt%, Aldrich Chemical Co.) and lithium hydroxide (Aldrich Chemical Co.) in a composition of $\text{Zn}(\text{C}_5\text{H}_7\text{O}_2)_2 \cdot \text{H}_2\text{O} : 2\text{H}_3\text{PO}_4 : 2\text{LiOH}$. The reaction mixture led to the formation of a gelatinous white precipitate. The precipitate was recovered by filtration and dried at 110°C for 2 h. The dry white powder was analyzed by

— X-ray powder diffraction (XRD) using a SCINTAG automated PAD-X diffractometer utilizing monochromatic $\text{CuK}\alpha$ radiation. The diffraction patterns were taken in the range of $5^\circ < 2\theta < 70^\circ$. The 2θ step size was 0.04° and the count time was 1 s. Quartz was used as an internal standard. Cell parameters were obtained from a least-squares refinement of the XRD data with the aid of a computer program, which corrected for the systematic experimental errors.

— Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) using a TG7/DSC Perkin-Elmer thermal analyzer connected to a thermal analysis system. Samples were heated at a rate of $10^\circ/\text{min}$ in a nitrogen atmosphere, with a gas flow rate of 25 ml/min. All the sample weights were in the 10- to 20-mg range.

— Fourier transform infrared (FTIR) spectroscopy using a Nicolet Impact 400 spectrometer in the wavelength range of $1400\text{--}400 \text{ cm}^{-1}$. The FTIR spectra were taken on KBr pellets. The spectra were composites of 64 individual scans and were all taken under a dry nitrogen atmosphere at room temperature.

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TABLE 1
X-ray Powder Diffraction Data of the As-Prepared Sample

<i>h</i>	<i>k</i>	<i>l</i>	<i>d</i> _{obs} (Å)	<i>d</i> _{calc} (Å)	<i>I</i> _{obs} (%)
1	0	0	8.0781	8.0126	12
0	1	1	7.8931	7.8463	25
1	1	-1	6.9536	6.9419	10
0	2	0	6.4771	6.5462	57
0	2	1	5.4534	5.4437	14
1	2	0	5.1216	5.0694	13
1	1	1	4.8387	4.8288	20
2	0	-1	4.4624	4.4465	26
2	1	-1	4.2997	4.2103	58
2	0	0	4.0452	4.0063	32
0	3	1	4.0229	3.9868	33
0	2	2	3.9860	3.9231	24
1	0	-3	3.6560	3.6260	19
1	1	-3	3.5477	3.4945	11
2	0	1	3.2355	3.2470	93
1	4	-1	3.0426	3.0392	100
3	0	-2	2.9580	2.9435	63
3	1	-2	2.8590	2.8718	14
0	4	2	2.7266	2.7218	10
3	2	-1	2.6666	2.6846	12
2	0	2	2.6374	2.5975	21

TABLE 1—Continued

<i>h</i>	<i>k</i>	<i>l</i>	<i>d</i> _{obs} (Å)	<i>d</i> _{calc} (Å)	<i>I</i> _{obs} (%)
2	4	-2	2.5271	2.5564	56
2	2	2	2.4103	2.4144	26
1	5	-2	2.3521	2.3510	18
3	3	0	2.2468	2.2781	15
2	5	-2	2.2027	2.2058	13
3	2	1	2.1964	2.2002	20
1	5	2	2.1045	2.1072	13
4	2	-1	2.0378	2.0468	20
4	1	0	1.9877	1.9801	14
2	6	-2	1.9395	1.9256	26
1	3	-5	1.8946	1.9139	18
3	3	2	1.8204	1.8235	50
2	4	3	1.7737	1.7796	20
4	5	-1	1.6704	1.6639	9
4	4	1	1.5843	1.5866	11

As-prepared sample	Na ₂ Zn(HPO ₄) ₂ ·4H ₂ O(10)	
<i>a</i> (Å)	8.896(8)	8.947(2)
<i>b</i> (Å)	13.092(5)	13.254(2)
<i>c</i> (Å)	10.882(9)	10.098(2)
<i>β</i> (°)	115.760(6)	116.358(6)

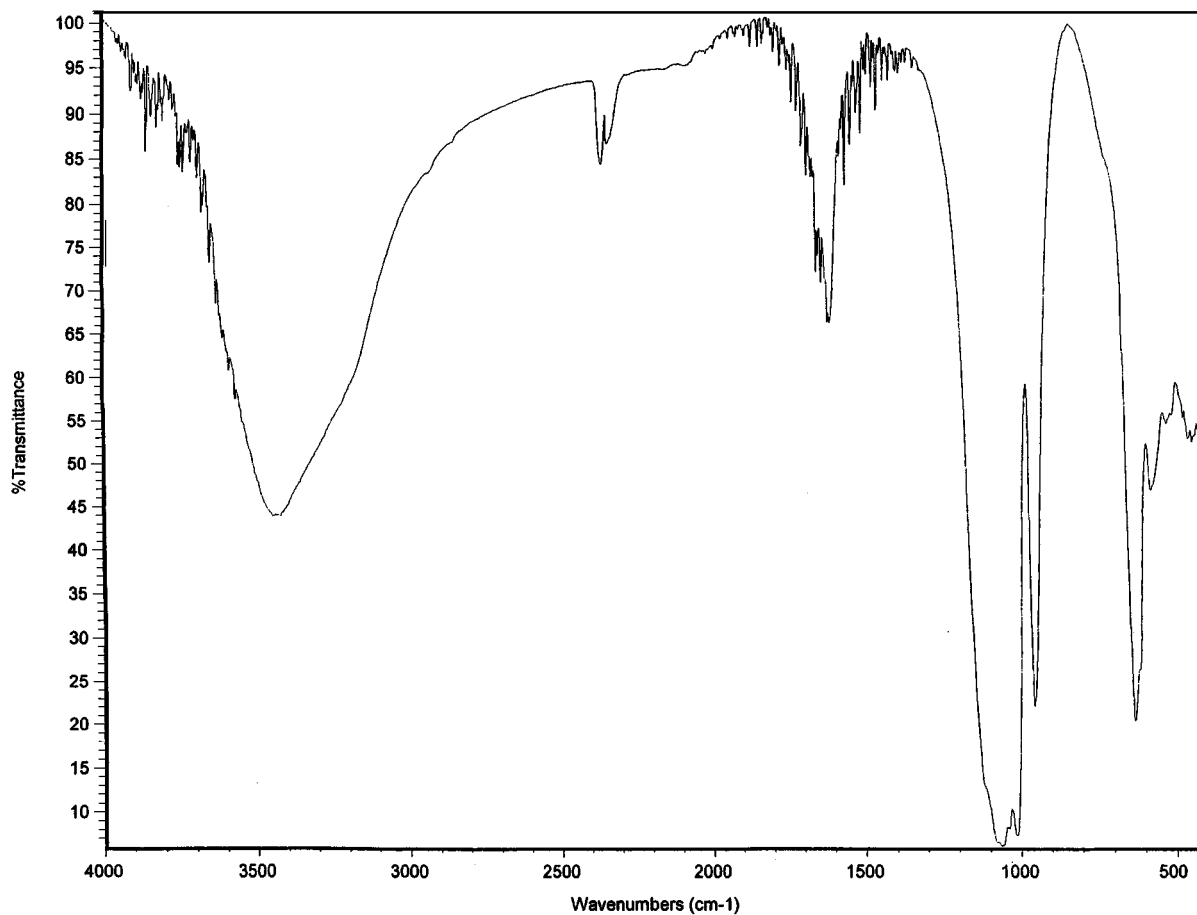


FIG. 1. FTIR spectrum of the as-prepared sample.

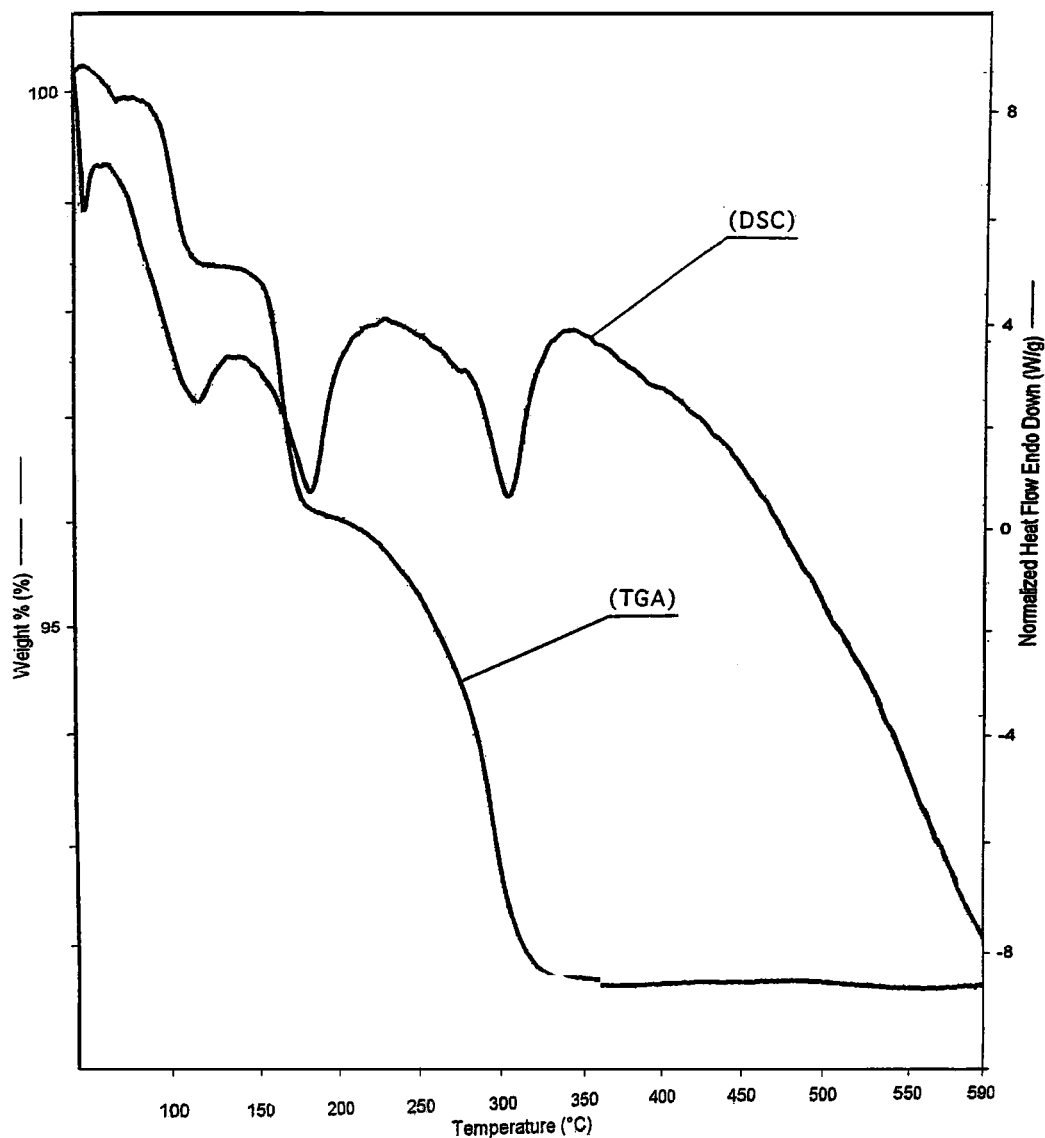


FIG. 2. DS-TG curve of the as-prepared sample.

RESULTS AND DISCUSSION

The X-ray powder diffraction pattern and the corresponding data indicate that the prepared solid is isostructural with $\text{Na}_2\text{Zn}(\text{HPO}_4)_2 \cdot 4\text{H}_2\text{O}$ (Table 1). Using a Scintag Indexing program, the XRD data were indexed in a monoclinic cell. The least-squares refinement of the indexed pattern gave a cell with dimensions $a = 8.896(8) \text{ \AA}$; $b = 13.092(5) \text{ \AA}$; $c = 10.882(9) \text{ \AA}$, and $\beta = 115.760(6)^\circ$. These cell dimensions are very similar to those of $\text{Na}_2\text{Zn}(\text{HPO}_4)_2 \cdot 4\text{H}_2\text{O}$. However, the c parameter of the prepared sample appears to be slightly larger.

The infrared spectrum of the as-prepared sample (Fig. 1) exhibits several OH vibrations. The bands observed at

1630 cm^{-1} and at 3250 cm^{-1} are attributed respectively to the water bending and stretching motions, while the band observed at 3450 cm^{-1} and the small shoulder at about 3600 cm^{-1} are both assigned to H-O(P) stretching in HPO_4^{2-} ions. The absorption bands observed in $400\text{--}700$ and $900\text{--}1250 \text{ cm}^{-1}$ are all assigned to the various vibration modes of HPO_4^{2-} ions.

X-ray data along with the IR observations confirm the isostructurality with $\text{Na}_2\text{Zn}(\text{HPO}_4)_2 \cdot 4\text{H}_2\text{O}$ of the prepared sample and therefore suggest the empirical formula $\text{Li}_2\text{Zn}(\text{HPO}_4)_2 \cdot n\text{H}_2\text{O}$. To confirm the exact amount of water of hydration and also study the thermal stability of the prepared sample, thermogravimetric analysis (TGA) as well as differential scanning calorimetry (DSC) were

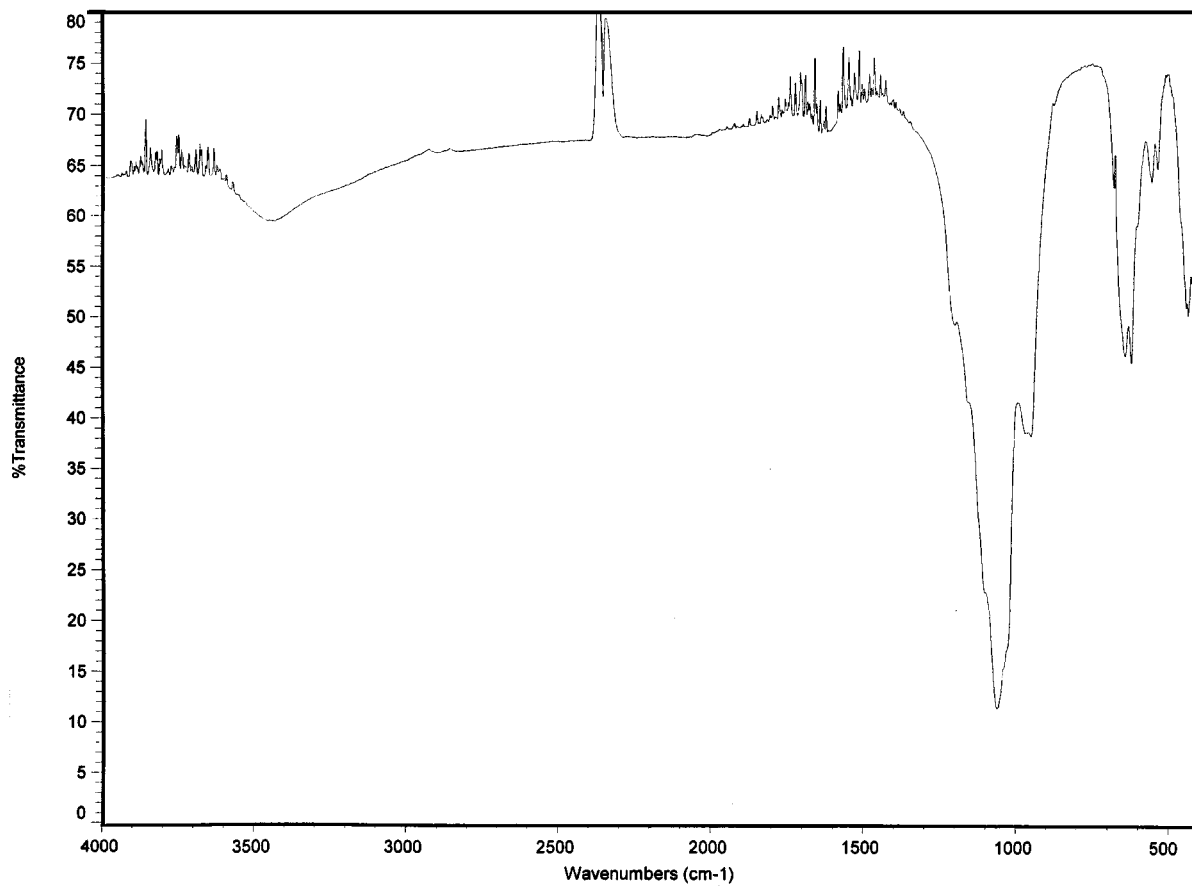


FIG. 3. FTIR spectrum of the as-prepared sample heated at 250°C.

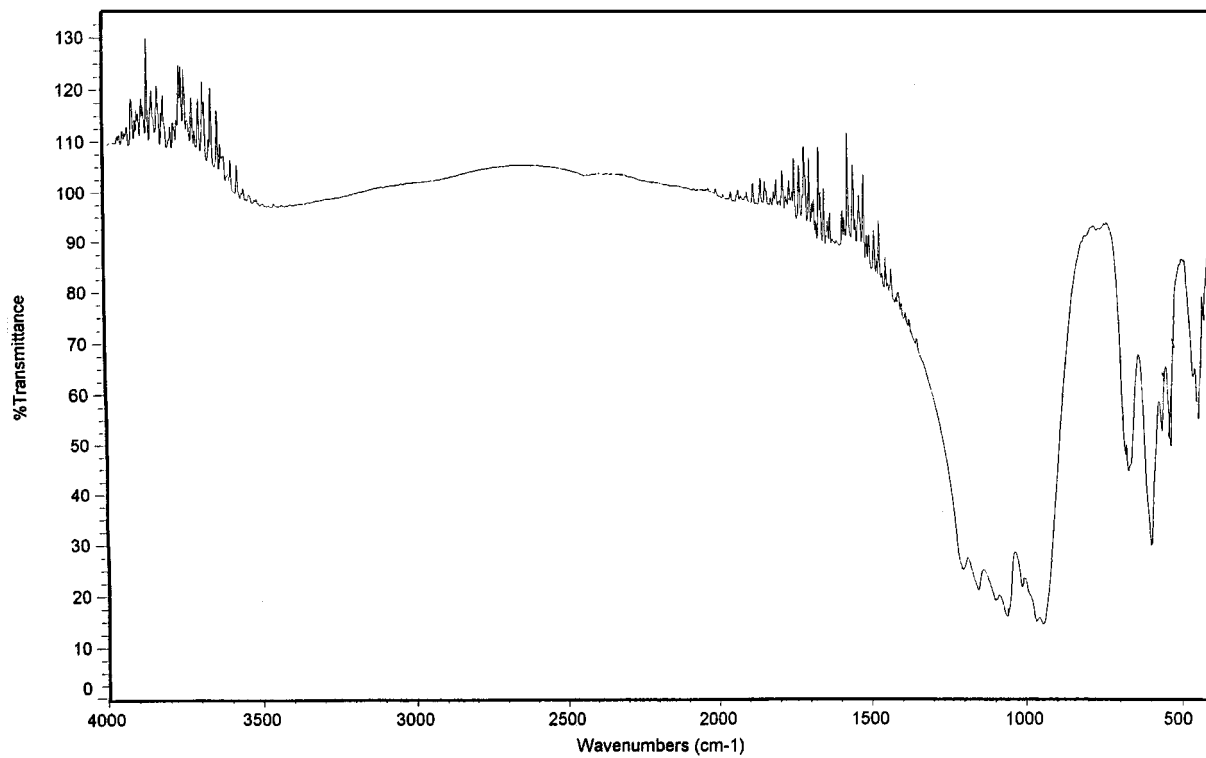


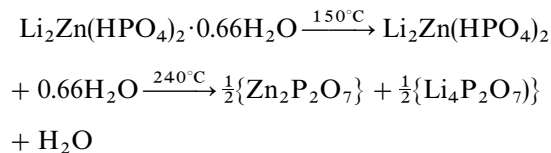
FIG. 4. FTIR spectrum of the as-prepared sample heated at 500°C.

performed. The DS-TG curve (Fig. 2) exhibits three endothermic effects corresponding to three weight losses. The first one occurs at around 100°C with a weight loss of 1.5% followed by the second one at around 150°C with a weight loss of 2.5%. The third weight loss of 4.5% is observed at 240°C. No weight change is observed beyond 350°C.

The total observed weight loss is 8.5%. The first two heat events can be attributed to the removal of water molecules intercalated in the structure. In fact, the IR spectra of the sample heated at 200°C show the disappearance of the O–H vibration attributed to water molecules (Fig. 3). The third weight loss, observed at 240°C, is attributed to the loss of water due to the dehydration of HPO_4^{2-} into $\text{P}_2\text{O}_7^{4-}$ ions. The XRD data of the sample heated at 500°C for 1 h shows that this HPO_4^{2-} – $\text{P}_2\text{O}_7^{4-}$ transformation leads to a mixed phase $\text{Zn}_2\text{P}_2\text{O}_7$ (11) $\text{Li}_4\text{P}_2\text{O}_7$ (12). This is also confirmed by the IR spectra of the sample heated at 500°C (Fig. 4). Indeed, it shows the disappearance of all the absorptions within 4000–3000 cm^{-1} and distinct changes for all the absorptions in the 1400 to 400- cm^{-1} range. Thus, by attributing the third weight loss to the dehydration of HPO_4^{2-} ions, we have used the first two weight losses to estimate the amount of water molecules intercalated in the structure. The composition of the as-prepared sample is then determined to be $\text{Li}_2\text{Zn}(\text{HPO}_4)_2 \cdot 0.66\text{H}_2\text{O}$.

The structural changes due to two consecutive loss of water by the prepared samples can be summarized in the

equations below:



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