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Ga(2,2′-bipy)(HPO$_4$)(H$_2$PO$_4$): First Layered Inorganic−Organic Hybrid Gallium Phosphate with a Neutral Framework

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A novel gallium phosphate, Ga(2,2′-bipy)(HPO$_4$)(H$_2$PO$_4$) (denoted FJ-12; FJ = Fujian Institute of Research on the Structure of Matter), which is the first example of layered inorganic−organic hybrid gallium phosphate with neutral framework, has been hydrothermally synthesized and structurally characterized by single-crystal X-ray diffraction. This compound crystallizes in the monoclinic system, space group $P2_1/c$ (No. 14), with $a = 10.9443(9)$, $b = 15.8253(13)$, and $c = 8.4201(7)$ Å, $\beta = 108.898(2)°$, $V = 1379.7(2)$ Å^3, and $Z = 4$. The structure consists of HPO$_4$ and H$_2$PO$_4$ tetrahedra and unusual GaO$_4$N$_2$ octahedra which are linked through their vertexes forming an undulated sheetlike structure with 4.12-net. The adjacent layers are stably packed together and exhibit interesting 3-D supramolecular arrays π–π interactions of the 2,2′-bipy groups.

Introduction

The research for novel microporous materials is very intense due to the potential application of these materials as absorbents, ion exchangers, and catalysts in heterogeneous catalysis.[1] Since the discovery of crystalline aluminophosphate molecular sieves in 1982,[2] a great deal of attention has been paid to the synthesis of open-framework phosphate-based materials.[3,4] The gallium phosphate family of solids has proved a particularly rich source of new compounds.[5−12] This is in part due to the ability of gallium to exist in a more variable and expanded coordination environment, as opposed to zeolites and aluminophosphates that only contain tetrahedrally coordinated units. One approach to the design and synthesis of novel materials in this system exploits the influence of organic amines on inorganic frameworks. Férey et al. reported the hydrothermal synthesis of a series of open-framework gallium phosphates (designated ULM-*n*) using several amines of varying chain lengths as templates.[13−16] An alternative approach to this method employs the organic component as a ligand, which was directly coordinated to the metal phosphate scaffolding.[17] Compared with inorganic ligands, organic multidentate ligands possess more rich coordination sites and a wide variety of shapes. One may expect that the rational design of crystalline solids with complex architectures may be realized through shrewd choice of organic species. The most famous example is the synthesis of NTHU-1, a novel porous gallium phosphate containing 24-ring channels.[18]

Metal phosphates with neutral layers are interesting with respect to intercalation reaction. For example, VOPO$_4$·2H$_2$O is a well-known layered metal phosphate that possesses a high ability to intercalate a wide range of guest molecules, including amine, amide, alcohol, carboxylic acid, amino acid, pyridine, and poly(ethylene oxide).[19,20] These intercalation

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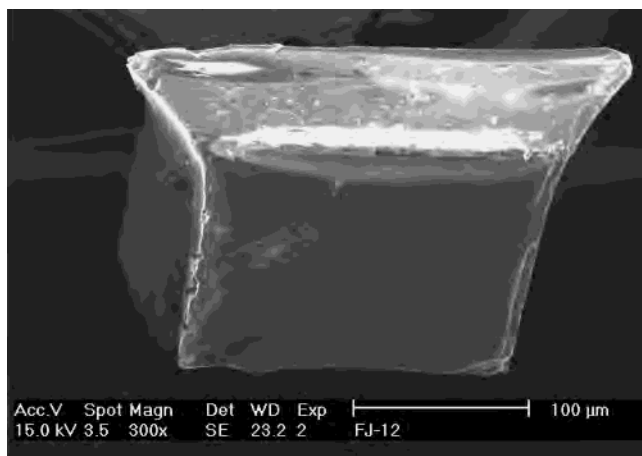(18) Lin, C.-H.; Wang, S.-L.; Lii, K.-H. *J. Am. Chem. Soc.* **2001**, *123*, 4649.

Figure 1. SEM image showing the morphology of a single crystal of as-synthesized FJ-12.

reactions may change the electronic properties of the host lattice, which indicates the practical use of these materials as sensors. To promote specific chemical reactions or to enhance particular physical properties, new types of layered materials are often desired.

A study of the literature of the inorganic−organic hybrid materials showed that 2,2′-bipyridine (2,2′-bipy) was a versatile organic ligand to construct appealing architecture of varying dimensions.[21] Others and we have reported the syntheses of hybrid solids in the 2,2′-bipy−phosphate system.[22−24] As part of our continuous work in this system, we report here a new hybrid solid, Ga(2,2′-bipy)-$(HPO_4)(H_2PO_4)$ (denoted FJ-12), which is built up by HPO_4, H_2PO_4, and GaO_4N_2 units via vertex oxygen atoms forming an undulated sheetlike structure with 4.12-net. To our knowledge, FJ-12 is the first example of a layered inorganic−organic hybrid gallium phosphate with a neutral framework.

Experimental Section

Synthesis. FJ-12 was synthesized by the hydrothermal method under autogenous pressure. In a typical synthesis, 0.10 g of Ga_2O_3 was dispersed in a mixture solution of 3.2 mL of water and 3.3 mL of ethylene glycol (EG); then 0.25 mL of H_3PO_4 (85 wt %) was added under constant stirring. To this mixture, 0.325 g of 2,2′-bipy was added, and the resulting mixture, with a pH of 4, was homogenized for 120 min at room temperature. The final mixture of the composition Ga_2O_3−H_3PO_4−2,2′-bipy−H_2O−EG in a molar ratio of 1:7:12.3:610:200 was sealed in a Teflon-lined steel autoclave, heated at 165 °C for 7 days, and then cooled to room temperature. The resulting product, consisting of colorless prismlike crystals (Figure 1), was recovered by filtration, washed with distilled water and alcohol, and finally dried at ambient temperature (83% yield based on gallium). We have also carried out some reactions without ethylene glycol in the reaction mixture. The resulting

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Table 1. Crystal and Structure Refinement Data for FJ-12

empirical formula	$C_{10}H_{11}GaN_2O_8P_2$
fw	418.87
space group	$P2_1/c$ (No. 14)
a, Å	10.9443(9)
b, Å	15.8253(13)
c, Å	8.4201(7)
β, deg	108.898(2)
V, Å³	1379.7(2)
Z	4
T, K	293(2)
λ(Mo Kα), Å	0.710 73
ρ_{calc}, g cm⁻³	2.016
μ(Mo Kα), mm⁻¹	2.273
R_1^a [$I > 2\sigma(I)$]	0.0752
wR_2^b [$I > 2\sigma(I)$]	0.1477

^{a} $R_1 = ||F_o| - |F_c||/\Sigma|F_o|$. ^{b} $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$, $w = 1/[\sigma^2(F_o^2) + (0.0494P)^2 + 15.79P]$, where $P = [|F_o|^2 + 2|F_c|^2]/3$.

product contained a major phase of colorless prism-shaped crystals of FJ-12 plus a tiny amount of unidentified powder. It seems that the use of EG in the synthesis improves the yield.

Characterization. The elemental analysis was carried out on an Elementar Vario EL III analyzer, and the inductively coupled plasma (ICP) analysis was carried out on a Perkin-Elmer Optima 3300 DV spectrometer. IR spectra (KBr pellets) were recorded on an ABB Bomen MB 102 spectrometer. The thermogravimetric analysis was performed on a Mettler Toledo TGA/SDTA 851e analyzer under different gases with a heating rate of 10 °C/min⁻¹ from 30 to 1000 °C. Powder X-ray diffraction (XRD) data were obtained using a Philips X'Pert-MPD diffractometer with Cu Kα radiation (λ = 1.540 56 Å). Qualitative energy dispersive spectroscopy (EDS) analysis on single crystals was performed on a Philips-FEI XL30 ESEM-TMP scanning electron microscope equipped with an EDAX system.

Determination of Crystal Structure. A suitable single crystal of as-synthesized compound with the dimensions of 0.16 × 0.14 × 0.08 mm was carefully selected under an optical microscope and glued to a thin glass fiber with epoxy resin. Crystal structure determination by X-ray diffraction was performed on a Siemens SMART CCD diffractometer with graphite-monochromated Mo Kα (λ = 0.710 73 Å) radiation in the ω and φ scanning mode at room temperature. An empirical absorption correction was applied using the SADABS program.[25] The structure was solved by direct methods. The gallium and phosphorus atoms were first located, and the carbon, nitrogen, and oxygen atoms were found in the final difference Fourier map. All the H atoms were placed geometrically. The structure was refined on F^2 by full-matrix least-squares methods using the SHELX97 program package.[26,27] All non-hydrogen atoms were refined anisotropically. The crystallographic data for FJ-12 are presented in Table 1. The coordinates of all non-H atoms and selected bond distances and angles are listed in Tables 2 and 3.

Results and Discussion

The experimental X-ray powder diffraction pattern of the bulk product was in good agreement with the simulated one on the basis of the single-crystal structure, as shown in Figure 2. The diffraction peaks on both patterns corresponded well in position, indicating the phase purity of the as-synthesized

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Ga(2,2′-bipy)(HPO₄)(H₂PO₄)

Table 2. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{Å}^2 \times 10^3$) for FJ-12

|	x	y	z	U(eq)
Ga	6697(1)	3854(1)	5453(1)	18(1)
P(1)	6442(2)	5825(2)	6258(3)	19(1)
P(2)	5636(2)	2141(2)	3132(3)	20(1)
O(1)	6524(6)	2745(4)	4341(8)	25(2)
O(2)	7112(6)	4981(4)	6497(8)	23(2)
O(3)	4999(6)	5808(4)	5868(8)	23(2)
O(4)	6389(7)	1520(4)	2429(8)	28(2)
O(5)	6818(7)	6289(5)	4859(10)	41(2)
O(6)	7048(7)	6322(5)	7930(9)	43(2)
O(7)	4929(7)	1594(4)	4129(9)	32(2)
O(8)	4586(6)	2570(4)	1692(8)	24(2)
N(1)	8640(8)	3579(5)	6507(11)	28(2)
N(2)	7438(7)	4264(5)	3566(10)	22(2)
C(1)	9199(11)	3272(7)	8045(15)	41(3)
C(2)	10519(12)	3150(8)	8733(17)	53(4)
C(3)	11299(12)	3344(8)	7760(20)	59(4)
C(4)	10735(11)	3657(8)	6184(19)	53(4)
C(5)	9403(10)	3760(6)	5562(14)	31(3)
C(6)	8711(10)	4100(6)	3889(13)	30(3)
C(7)	9299(13)	4259(9)	2648(18)	53(4)
C(8)	8534(17)	4566(8)	1104(17)	58(4)
C(9)	7265(15)	4740(9)	847(16)	55(4)
C(10)	6751(11)	4584(7)	2098(13)	34(3)

[a] U(eq) is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for FJ-12[a]

Ga−O(4)[#1]	1.897(7)	N(1)−C(1)	1.331(14)
Ga−O(3)[#2]	1.906(6)	N(1)−C(5)	1.357(13)
Ga−O(1)	1.968(6)	N(2)−C(10)	1.322(13)
Ga−O(2)	1.976(6)	N(2)−C(6)	1.355(13)
Ga−N(1)	2.068(8)	C(1)−C(2)	1.385(16)
Ga−N(2)	2.107(8)	C(2)−C(3)	1.40(2)
P(1)−O(2)	1.505(7)	C(3)−C(4)	1.361(19)
P(1)−O(3)	1.505(6)	C(4)−C(5)	1.390(15)
P(1)−O(5)	1.553(7)	C(5)−C(6)	1.469(15)
P(1)−O(6)	1.560(7)	C(6)−C(7)	1.416(15)
P(2)−O(1)	1.502(7)	C(7)−C(8)	1.386(19)
P(2)−O(4)	1.520(7)	C(8)−C(9)	1.36(2)
P(2)−O(8)	1.533(7)	C(9)−C(10)	1.368(16)
P(2)−O(7)	1.572(7)		
O(4)[#1]−Ga−O(3)[#2]	100.5(3)	O(2)−P(1)−O(5)	106.5(4)
O(4)[#1]−Ga−O(1)	97.0(3)	O(3)−P(1)−O(5)	111.1(4)
O(3)[#2]−Ga−O(1)	92.7(3)	O(2)−P(1)−O(6)	106.3(4)
O(4)[#1]−Ga−O(2)	88.4(3)	O(3)−P(1)−O(6)	108.4(4)
O(3)[#2]−Ga−O(2)	92.6(3)	O(5)−P(1)−O(6)	107.9(5)
O(1)−Ga−O(2)	171.6(3)	O(1)−P(2)−O(4)	111.2(4)
O(4)[#1]−Ga−N(1)	90.5(3)	O(1)−P(2)−O(8)	114.1(4)
O(3)[#2]−Ga−N(1)	169.0(3)	O(4)−P(2)−O(8)	109.9(4)
O(1)−Ga−N(1)	86.8(3)	O(1)−P(2)−O(7)	108.1(4)
O(2)−Ga−N(1)	86.7(3)	O(4)−P(2)−O(7)	105.9(4)
O(4)[#1]−Ga−N(2)	168.3(3)	O(8)−P(2)−O(7)	107.1(4)
O(3)[#2]−Ga−N(2)	90.8(3)	P(2)−O(1)−Ga	146.2(4)
O(1)−Ga−N(2)	85.3(3)	P(1)−O(2)−Ga	135.2(4)
O(2)−Ga−N(2)	88.2(3)	P(1)−O(3)−Ga[#2]	151.3(4)
N(1)−Ga−N(2)	78.2(3)	P(2)−O(4)−Ga[#3]	144.7(4)
O(2)−P(1)−O(3)	116.4(4)		

[a] Symmetry transformations used to generate equivalent atoms: #1, x, $-y + 1/2$, $z + 1/2$; #2, $-x + 1$, $-y + 1$, $-z + 1$; #3, x, $-y + 1/2$, $z - 1/2$.

sample. ICP analysis for the product gave the contents of Ga 16.18 wt % (calcd 16.64 wt %) and P 14.27 wt % (calcd 14.79 wt %), indicating a Ga:P ratio of 1:2. The presence of gallium and phosphorus was also confirmed by EDS analysis on single crystals of FJ-12. Elemental analysis showed that the sample contains 28.35, 2.53, and 6.61 wt % of C, H, and N, respectively, in accord with the expected values of 28.67, 2.65, and 6.69 wt % of C, H, and N on the basis of
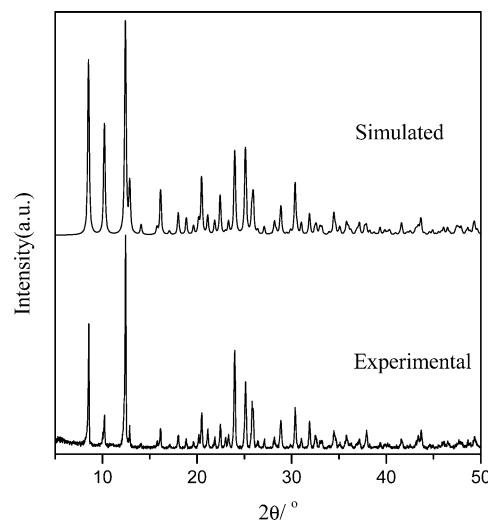
Figure 2. Experimental and simulated X-ray powder diffraction pattern of FJ-12.
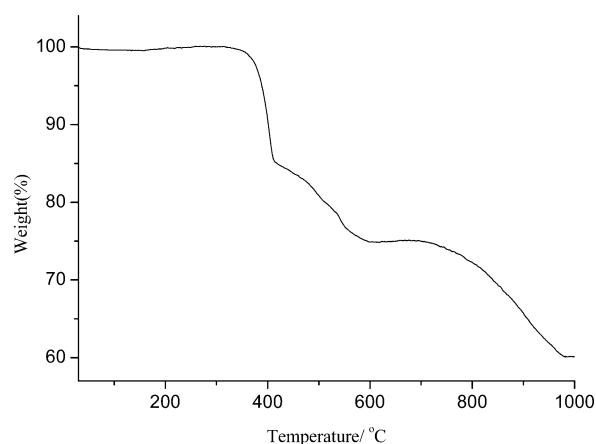
Figure 3. TG curve of FJ-12 under flowing air with a heating rate of 10 °C/min.

the empirical formula given by the single-crystal structure analysis.

The IR spectrum of the sample showed the stretching vibrations of C−H and N−H bands at 3122, 3065, and 3042 cm⁻¹, and the bands at 1615, 1603, 1578, 1497, 1479, 1446, and 1314 cm⁻¹ were assigned to the pyridine ring-stretching vibrations. The bands at 1130, 1107, 1033, and 989 cm⁻¹ were caused by the stretching vibrations of P−O bonds.

Initial thermogravimetric analysis of FJ-12 was carried out in a flow of dry air with a heating rate of 10 °C/min. As indicated by the TG curve shown in Figure 3, the structure remained stable up to ∼310 °C. On further heating, a two-step weight loss was observed. The initial weight loss between 310 and 600 °C should correspond to the departure of 2,2′-bipy ligands (calcd 37.29% weight loss for one 2,2′-bipy molecule/formula unit). However, the observed weight loss (25.17%) was much lower than the expected value. The lower reduction in this stage was due to the retention of carbon in the solid residue (black in color). The second step, occurring between 700 and 980 °C, with a weight loss of 14.84% should be attributed to the removal of carbon from the black solid residue. The total observed weight loss (40.01%) for the two steps compared well with that
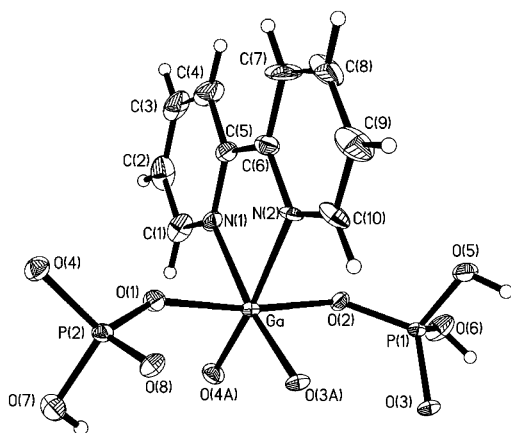
Figure 4. ORTEP view of the coordination environments of the gallium and phosphorus atoms in FJ-12, with 30% thermal ellipsoids and the atom-labeling scheme.

Figure 5. View of the layered structure of FJ-12 showing the 4,12-network: GaO_4N_2, medium gray; P-centered tetrahedra, white. All the carbon atoms are omitted for clarity.

Figure 6. Polyhedral view of the packing of layers along the [100] direction: GaO_4N_2, medium gray; P-centered tetrahedra, white.

calculated on the basis of the above interpretation. The XRD patterns of the post residue corresponded to dense $GaPO_4$ (crystobalite form) together with an amorphous phase. The same results were obtained in a flow of nitrogen as well.

The asymmetric unit of FJ-12 contains 23 independent atoms, including 1 gallium atom, 2 phosphorus atoms, 8 oxygen atoms, 10 carbon atoms, and 2 nitrogen atoms, as shown in Figure 4. The gallium atom is coordinated by two nitrogen atoms from a 2,2′-bipy ligand and four oxygen atoms to form an octahedral geometry. The Ga−O(N) bond distances are in the range of 1.897(7)−2.107(8) Å (average Ga−O(N) = 1.987 Å). The gallium atom is connected to two distinct P atoms via Ga−O−P links. Each of the two independent P atoms makes two P−O−Ga linkages and has two terminal P−O bonds. The P−O bond distances are in the range 1.502(7)−1.572(7) Å (average P(1)−O = 1.531 Å and P(2)−O = 1.532 Å). The framework stoichiometry of GaP_2O_8 creates a net charge of −3. Charge-balancing criterion requires the presence of three protons associated with the P−O bonds. Bond valence sum values clearly indicate that P(1)−O(5), P(1)−O(6), and P(2)−O(7) with distances of 1.553(7), 1.560(7), and 1.572(7) Å are P−OH units.[28] The remaining terminal linkage, in the case of P(2) with a P−O distance of 1.533(7) Å, is a P=O unit.

The network structure of FJ-12 consists of GaO_4N_2 octahedra and HPO_4 and H_2PO_4 tetrahedra linked through their vertexes. The connectivity of these units creates 4- and 12-membered rings along a-axis, as shown in Figure 5. Each 4-membered ring is surrounded by four 12-membered rings, while each 12-membered ring is surrounded by four 4-membered rings and four 12-membered rings. The 4-membered rings as building blocks, formed by alternating GaO_4N_2 and H_2PO_4 groups, are linked together through HPO_4 groups via Ga−O−P bonds, forming infinite layered structure. The formation of this unusual 4.12-net structure may be attributed to the aromatic organonitrogen ligand, 2,2′-bipy, which binds in a bidentate fashion to the octahedral gallium centers.

The adjacent layers are stacked in an AAAA sequence along the a-axis, as shown in Figure 6. 2,2′-bipy molecules are attached directly to Ga atoms within the layers by cov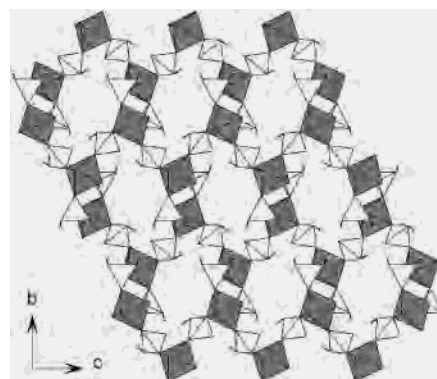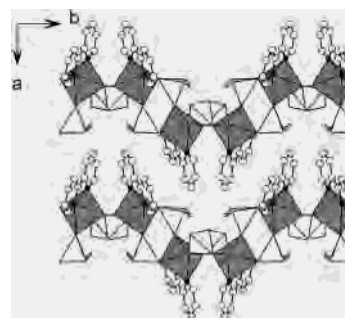alent bonds and protrude into the interlayer region. These aromatic organonitrogen ligands between adjacent layers are parallel with each other, and there are possible $\pi \cdots \pi$ interactions between them as reflected in an average distance of 3.39 Å. It is noted that there are no H-bonds between adjacent layers.

To date, four types of layered gallium phosphate have been synthesized in the presence of different structure-directing agents.[29−32] Interestingly, all the known 2-D gallium phosphates consist of macroanionic sheets with the guest templating agents intercalating between the inorganic layers and contact with inorganic sheets by strong H-bonding. The synthesis of FJ-12 provides a new type of layered gallium phosphate with neutral framework. It is worth noting that compounds with neutral layers are characterized by weak interlayer interactions such that they may accommodate large guest molecules by free adjustment of interlayer separation. Thus, the synthesis of this type of layered materials in which organic ligands are covalently linked to the layers may offer the prospect of some interesting new systems.

Conclusions

In summary, the synthesis, crystal structure, and thermal properties of a novel hybrid gallium phosphate, Ga(2,2′-

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bipy)(HPO_4)(H_2PO_4), have been described. The structure consists of GaO_4N_2 octahedra, HPO_4 and H_2PO_4 tetrahedra, and 2,2′-bipy ligands. The strict alternation of Ga-centered octahedra (GaO_4N_2) and P-centered tetrahedra (HPO_4 and H_2PO_4) forms a 2-D sheet architecture with 4.12-net parallel to the *bc*-plane. The 2,2′-bipy ligands are directly coordinated to the puckered layers and extend the 2-D layer into a 3-D supramolecular array via $\pi-\pi$ interactions. It is noteworthy that, in the reported organonitrogen-ligated gallium phosphates, gallium atoms are present in both four- and six-coordinate environments. However, all of the gallium atoms in FJ-12 are six-coordinated. The successful synthesis of this compound provides the possibility for preparing new types of layered material that may find widespread application in intercalation reactions.

Supporting Information Available: Crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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