A novel copper diphosphonate complex $Cu_4(aedp)_2(4,4'\text{-bpy})(H_2O)_4$ with three-dimensional framework structure

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Abstract

A novel copper organodiphosphonate complex containing a second ligand 4,4′-bipyridine (4,4′-bpy) based on 1-aminoethylidene-diphosphonic acid (H_4aedp), $Cu_4(aedp)_2(4,4'\text{-bpy})(H_2O)_4$ (**1**), has been synthesized under hydrothermal conditions. Complex **1** adopts a three-dimensional framework structure assembled from $\{Cu_4(aedp)_2(H_2O)_4\}$ layers and 4,4′-bpy bridges. Each $\{Cu_4(aedp)_2(H_2O)_4\}$ unit consists of three crystallographically distinct Cu atoms. The Cu(1) atom has a distorted square pyramidal geometry, whereas the Cu(2) and Cu(3) atoms have a distorted elongated tetragonal octahedral geometry. The magnetic studies indicate that complex **1** show typical antiferromagnetic behaviors at low temperature, which is attributed to the superexchange couplings between Cu(II) centers through μ–O bridge in the phosphonate layers. Crystal data for **1**: triclinic, space group $P\bar{1}$, $a = 8.0931(16)$, $b = 13.567(3)$, $c = 6.2185(12)$Å, $\alpha = 90.55(3)$, $\beta = 96.97(3)$, $\gamma = 78.50(3)^\circ$, $V = 664.1(2)$Å^3, $Z = 2$.
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1. Introduction

Recently, increased attention has been focused on the design and assembly of multifunctional coordination compounds, particularly the self-assembly of metal phosphonates with one-, two- or three-dimensional structures due to their potential applications in magnetic materials, sorption, catalysis, ion exchange, protonic conductor and sensors [1–6]. Great efforts have been devoted to the syntheses of metal phosphonate compounds with novel open-framework or microporous structures [7–12]. The diphosphonic acids have been proved to be good candidates for the synthesis of open-framework or porous materials, in which the organic part plays a controllable spacer role and the two inorganic –PO$_3$ groups chelate with metal ions to form one-, two-, or three-dimensional structures. We have been interested in exploring novel metal phosphonate compounds based on 1-aminoethylide-nediphosphonic acid (H_4aedp). In order to construct three-dimensional structures, we tried to introduce a second bridging ligand into the system. Fortunately the compound $Cu_4(aedp)_2(4,4'\text{-bpy})(H_2O)_4$ was prepared successfully. Herein we report the syntheses and characterizations of a new copper phosphonate containing 4,4′-bipyridine (4,4′-bpy) namely $Cu_4(aedp)_2(4,4'\text{-bpy})(H_2O)_4$ (**1**) (aedp = $CH_3C(NH_2)(PO_3)_2$, 4,4′-bpy = 4,4′-bipyridine). Its structure is different from compounds $(NH_4)Cu_3(hedp)_2(H_2O)_4$ [13] and $[Cu_3(hedpH)_2(4,4'\text{-bipy})(H_2O)_2] \cdot 2H_2O$ [12] where the similar diphosphonic acid is employed. As far as we know, no example of metal-aedp-4,4′-bpy compounds has been structurally determined so far.

2. Experimental section

2.1. Materials and methods

All chemicals were of reagent quality obtained from commercial sources and used without further purification.

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The ligand H_4aedp was prepared according to an improved method of the literature [14]. The elemental analyses were performed on a Carlo-Erba 1160 elemental analyzer. The infrared spectra were recorded on a Shimadzu IR 435 spectrometer with pressed KBr pellets. Thermal analyses were performed in nitrogen in the temperature range 30–1100 °C with a heating rate of 10 °C min^{-1} on a NETZSCH STA 409 PC/PG instrument. Variable temperature magnetic susceptibility data were obtained on a polycrystal sample from 5 to 300 K in a magnetic field of 500 G using a SQUID Quantum Design MPMS-5 magnetometer. Diamagnetic corrections were estimated from Pascal's constants [15].

2.2. Synthesis of $Cu_4(aedp)_2(4,4'-bpy)(H_2O)_4$ (1)

A mixture of $Cu(NO_3)_2 \cdot 3H_2O$ (1 mmol, 0.2415 g), H_4aedp (1 mmol, 0.2050 g), 4,4'-bpy (1 mmol, 0.1560 g) and H_2O (10 cm^3) was kept in a Teflon-lined stainless steel container at 160 °C for 2 d. After the mixture was slowly cooled to room temperature with the cooling rate of 5 °C/h, blue needle-like crystals were obtained together with a small amount of unidentified white flocculent material. The blue crystals were manually isolated for structural measurement and the physical property measurements. Yield: 35% based on Cu. Anal. Found (%): C, 18.32; H, 4.01; N, 6.04. Calcd. for $C_7H_{19}Cu_2N_2O_8P_2$: C, 18.75; H, 4.24; N, 6.25. IR (KBr, cm^{-1}): 3443s, 3166s, 2931s, 2752m, 1611s, 1539w, 1490w, 1452w, 1414m, 1222m, 1124vs, 1065vs, 1006vs, 962m, 812m, 728m, 668m, 587s, 508w, 418w.

2.3. X-ray crystallographic analysis

Single crystal with dimensions $0.20 \times 0.18 \times 0.16$ mm for **1** was selected for indexing and intensity data collection. The intensity data were collected on a Rigaku RAXIS-IV image plate area detector with graphite monochromated Mo$K\alpha$ radiation ($\lambda = 0.71073$ Å) at 291(2) K. The structure was solved by direct methods and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. The hydrogen atoms were included but not refined. The final cycle of full-matrix least-squares refinement was based on the observed reflections and variable parameters. All calculations were performed using the SHELX-97 crystallographic software package [16]. The crystallographic and refinement details are listed in Table 1. Complete crystallographic data for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC 258471. Copy of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge, CB2 IEZ, UK (Fax: +44 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk).

Table 1
Crystallographic data for compound **1**

Empirical formula	$C_7H_{19}Cu_2N_2O_8P_2$
F_w	448.21
Crystal system	Triclinic
Space group	$P\bar{1}$
a (Å)	8.0931(16)
b (Å)	13.567(3)
c (Å)	6.2185(12)
α (deg.)	90.55(3)
β (deg.)	96.97(3)
γ (deg.)	78.50(3)
V (Å^3)	664.1(2)
Z	2
μ (mm^{-1})	3.484
D_c (g cm^{-3})	2.212
F (000)	442
Goodness-of-fit on F^2	1.045
R_1, wR_2 ($I > 2\sigma(I)$)	0.0797, 0.2188
R_1, wR_2 (all data)	0.0879, 0.2266
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	1.082, −1.602

$R_1 = \sum ||Fo| - |Fc|| / \sum |Fo|$; w$R_2 = \left[\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2 \right]^{1/2}$.

Table 2
Selected bond lengths (Å) and angles (deg.) for compound **1**

Cu(1)–O(1)	2.433(8)	Cu(1)–O(3)	1.908(7)
Cu(1)–O(5)	1.964(6)	Cu(1)–O(2)♯1	1.896(7)
Cu(1)–N(1)	2.003(8)	Cu(2)–O(4)♯2	1.984(7)
Cu(2)–O(4)	1.984(7)	Cu(2)–O(6)♯2	1.916(6)
Cu(2)–O(6)	1.916(6)	Cu(2)–N(2)	2.510(6)
Cu(2)–N(2)♯2	2.510(6)	Cu(3)–O(7)♯3	1.896(6)
Cu(3)–O(7)	1.896(6)	Cu(3)–O(8)	2.026(8)
Cu(3)–O(8)♯3	2.026(8)	Cu(3)–O(1)	2.531(8)
P(1)–O(2)	1.515(7)	P(1)–O(4)	1.526(8)
P(1)–O(3)	1.510(7)	P(2)–O(5)	1.530(6)
P(2)–O(6)	1.524(7)	P(2)–O(7)	1.504(7)
O(2)♯1–Cu(1)–O(3)	162.9(3)	O(2)♯1–Cu(1)–O(5)	89.1(3)
O(2)♯1–Cu(1)–N(1)	87.8(3)	O(3)–Cu(1)–O(5)	93.3(3)
O(3)–Cu(1)–N(1)	87.6(3)	O(3)–Cu(1)–O(1)	93.2(3)
O(2)♯1–Cu(1)–O(1)	103.7(3)	O(5)–Cu(1)–N(1)	172.2(3)
O(5)–Cu(1)–O(1)	90.8(3)	N(1)–Cu(1)–O(1)	96.9(3)
O(6)–Cu(2)–O(4)	89.7(3)	O(6)♯2–Cu(2)–O(4)	90.3(3)
O(6)♯2–Cu(2)–O(6)	180.0(1)	O(4)♯2–Cu(2)–O(4)	180.0(1)
O(7)–Cu(3)–O(8)	88.4(3)	O(7)♯3–Cu(3)–O(8)	91.6(3)
O(8)♯3–Cu(3)–O(8)	180.0(5)	O(7)♯3–Cu(3)–O(7)	180.0(1)
P(1)–O(2)–Cu(1)♯5	145.2(5)	P(1)–O(3)–Cu(1)	129.6(4)
P(1)–O(4)–Cu(2)	118.2(4)	P(2)–O(5)–Cu(1)	131.2(4)
P(2)–O(6)–Cu(2)	120.5(4)	P(2)–O(7)–Cu(3)	133.9(5)

Symmetry transformations used to generate equivalent atoms: ♯1 x, y, $z+1$; ♯2 $-x+2$, $-y+1$, $-z-1$; ♯3 $-x+3$, $-y+1$, $-z$; ♯5 x, y, $z-1$.

3. Results and discussion

3.1. Crystal structure of $Cu_4(aedp)_2(4,4'-bpy)(H_2O)_4$ (1)

The selected bond lengths and angles for compound **1** are listed in Table 2. Compound **1** crystallizes in triclinic, space group $P\bar{1}$. Fig. 1 shows a building unit of the

structure with atomic labeling scheme. Clearly, three kinds of copper atoms are crystallographically distinguished, among which Cu(1) atom has a distorted square pyramidal geometry with four binding sites in the equatorial plane provided by O(3), O(5), O(2B) from two equivalent aedp^{4-} groups and N(1) from 4,4-bpy. The apical position is occupied by O(1) from the water molecule. The mean deviation of the equatorial plane is 0.0173 Å, with the largest deviation of 0.0347 Å at O(3). The Cu(1) atom is pulled out of the equatorial plane by 0.1421 Å. All the Cu(1)–O and Cu(1)–N bond lengths are normal except that the Cu(1)–O(1) is up to 2.433(8) Å. Both Cu(2) and Cu(3) atoms, which located on inversion center, are in approximately distorted tetragonal octahedral environments. The Cu(2) atom is coordinated by four oxygens [O(4), O(6), O(4A) and O(6A)] and two nitrogen atoms [N(2), N(2A)] from two equivalent aedp^{4-} groups . The Cu(2)–O bond lengths fall in the range 1.984(7)–1.916(6) Å. The Cu(3) atom is surrounded by four water molecules [O(8), O(8B),

O(1B), O(1C)] and two oxygen atoms [O(7), O(7B)] from the two equivalent aedp^{4-} groups.

In compound **1**, the aedp group bridges the Cu(1) and Cu(2) atoms through the bis(bidentate) mode, using four oxygen atoms [O(3), O(4), and O(5), O(6)] from its two {CPO$_3$} moieties. As a result, [Cu$_3$(aedp)$_2$(H$_2$O)$_2$]$^{2-}$ trimeric units are constructed. The neighboring trimers are fused together by the coordination of the phosphonate oxygen O(2) to the equivalent Cu(1) atom, hence forming an infinite double chain with a ladder-like motif along the *c*-axis (Fig. 2). These chains are connected through {Cu(3)O$_6$} units by sharing the remaining phosphonate oxygen O(7) of aedp ligand, leading to a two-dimensional network structure of copper phosphonate in the *ac* plane (Fig. 3). The layers are further linked by 4.4′-bpy bridging ligands, thus forming a three-dimensional framework structure, as shown in Fig. 4.

The structure of compound **1** is different from the other copper phosphonates such as (NH$_4$)Cu$_3$(hedp)$_2$(H$_2$O)$_4$ [13]
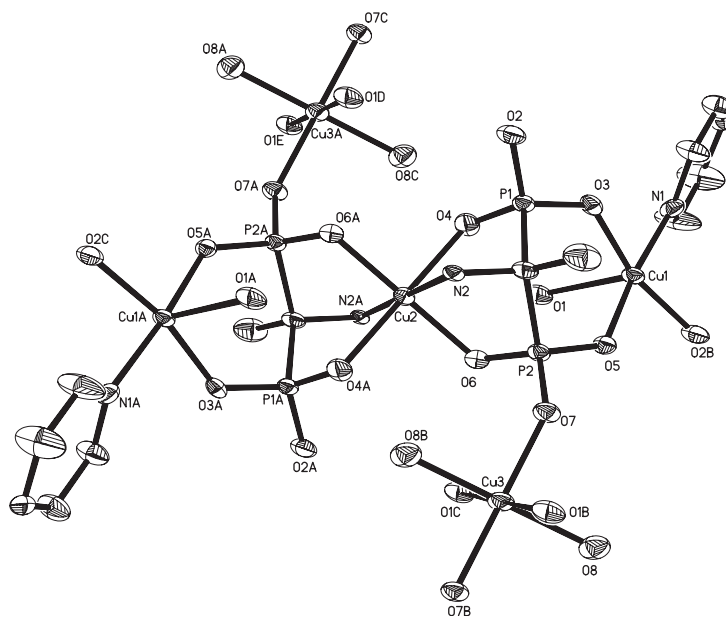

Fig. 1. The coordination spheres around Cu atoms in **1** (50% probability). All the H atoms are omitted for clarity.
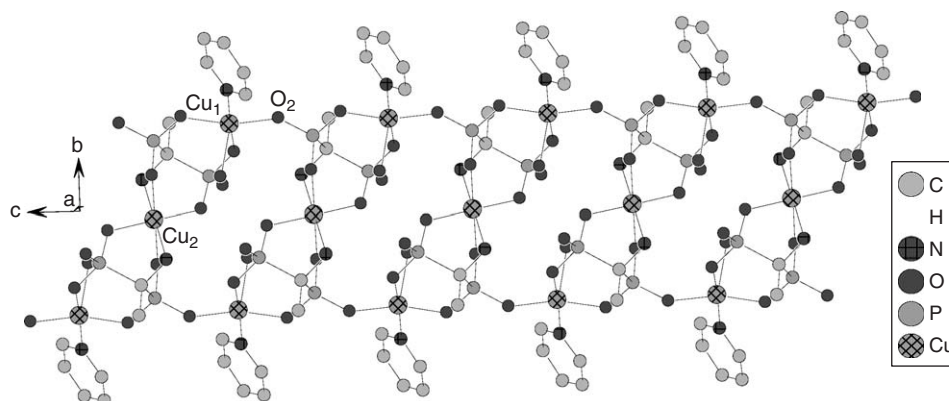

Fig. 2. A fragment of the chain composed of Cu(1) and Cu(2) atoms in **1**. All the H atoms are omitted for clarity.
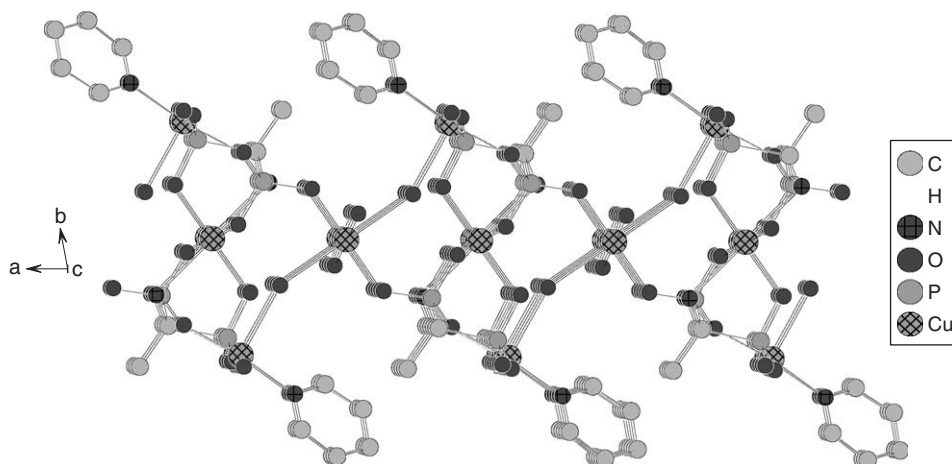
Fig. 3. A fragment of the two-dimensional layer viewed along the *c*-axis. All the H atoms are omitted for clarity.
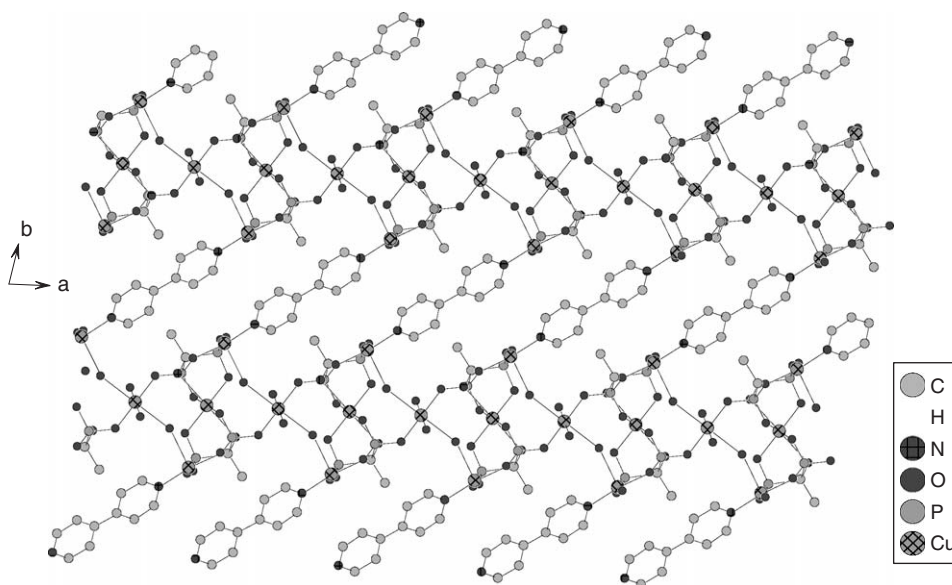

Fig. 4. Structure of compound **1** packed along the *c*-axis. All the H atoms are omitted for clarity.

and $[Cu_3(hedpH)_2(4,4'-bipy)(H_2O)_2] \cdot 2H_2O$ [12], although the chains of these compounds are also made up of $[Cu_3(hedp)_2(H_2O)_2]^{2-}$ trimeric units. In compound **1**, these $[Cu_3(aedp)_2(H_2O)_2]_n$ chains are connected through $\{Cu(3)O_6\}$ units, while the phenomenon could not be observed in the structure of $(NH_4)Cu_3(hedp)_2(H_2O)_4$ and $[Cu_3(hedpH)_2(4,4'-bipy)(H_2O)_2] \cdot 2H_2O$.

3.2. IR spectra and thermal analysis

The infrared spectra of compound **1** shows a series of strong bands in the 1200–920 cm^{-1} range, which are attributed to the stretching vibrations of –PO$_3$ groups [17]. The broad strong bands in the range 3000–3500 cm^{-1} are assigned as OH stretching vibrations of coordinated water molecules. The sharp bands at about 2930 and 2750 cm^{-1} are due to the –CH$_3$ group. The bands at about 1611 and 1452 cm^{-1} of compound **1** can be assigned to the characteristic C=C, C=N stretching vibrations of 4,4'-bpy. The complete deprotonation of the diphosphonate acid in **1** is confirmed by the absence of the –OH stretching vibrations of –POH at 2700–2500 and 2350–2100 cm^{-1} [18]. The thermal analysis shows several steps of decomposition in the temperature range 30–1100 °C (Fig. 5). The weight loss (7.1%) in the temperature range 30–220 °C correspond to the release of two molecules of water (calcd. 7.8%). Further weight loss (7.8%) between 220 and 306 °C is in agreement with the removal of the other two lattice water molecules (calcd. 7.8%). The weight loss above 306 °C is due to the decomposition of the organophosphonate ligand and the collapse of the lattice structure. The final product was not characterized.
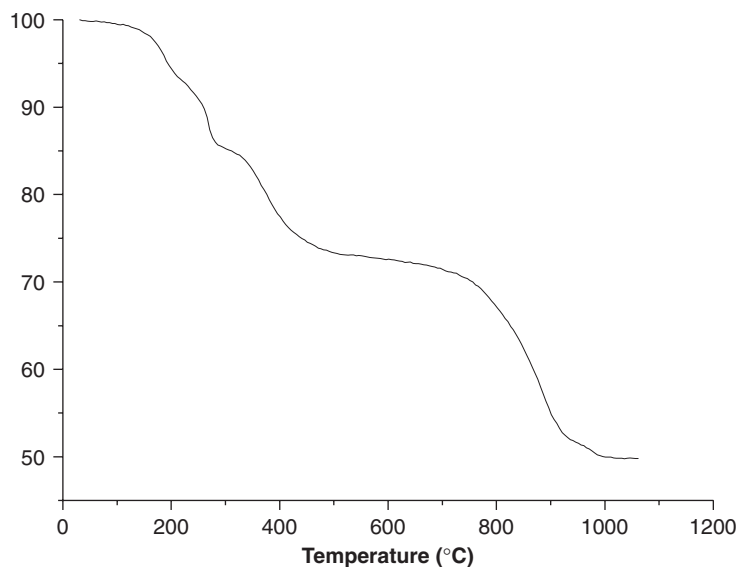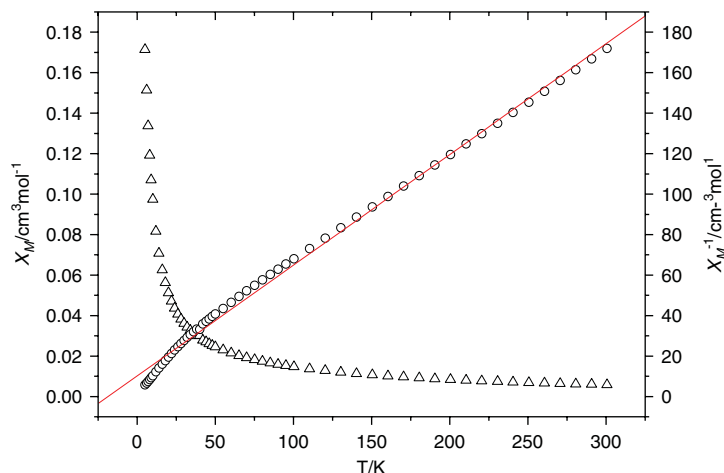
Fig. 5. TGA curve of the compound **1**.

Fig. 6. χ_m and $1/\chi_m$ vs. T plot for compound **1**.

3.3. Magnetic properties

The temperature-dependent molar magnetic susceptibilities of compound **1** were investigated in the temperature range 5–300 K (Fig. 6).

The value of $\chi_m T$ at 300 K is 1.70 cm^3 mol^{-1} K, which is higher than the expected value 1.5 cm^3 mol^{-1} K for four spin-only Cu(II) atoms ($S = 1/2$), attributing to the orbital contribution of the copper ion. On cooling from 300 K, the gradual decreasing of $\chi_m T$ indicates a characteristic antiferromagnetic interaction, which is also confirmed by a negative Weiss constant ($\theta = -27.1$ K) determined by the Curie–Weiss law $\chi_m = C/T - \theta$ in the temperature range 16–300 K. As described, the structure of **1** consists of $[Cu_4(aedp)_2(H_2O)_4]_n$ layers connected by 4,4′-bpy bridges, the Cu$\cdots$Cu distance over the μ–O(1) bridge (4.964 Å) is much shorter than those over the O–P–O bridges (6.84−6.928 Å). So the weak antiferromagnetic behavior is mainly attributed to the superexchange couplings between Cu(II) centers through μ–O(1) bridge in the phosphonate layers.

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