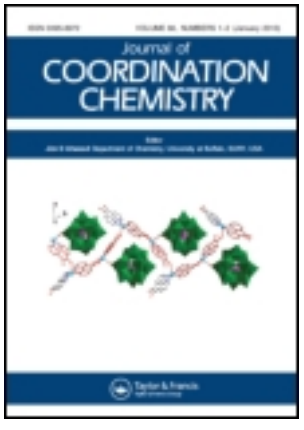

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Synthesis, characterization, and antitumor activities of two copper(II) complexes with pyrazole derivatives

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Two mononuclear copper(II) complexes with pyrazole derivatives, 1,1′-(anthracen-9-ylmethylene)bis(1H-pyrazole) (**L**[1]) and 9-(4-(di(1H-pyrazol-1-yl)methyl)phenyl)-9H-carbazole (**L**[2]), of formulae $[CuL^1(CH_3CN)_2](ClO_4)_2$ (**1**) and $[CuL^2(CH_3CN)_2](ClO_4)_2$ (**2**) were prepared. Both complexes were confirmed by IR, MS, ^1H NMR, and elemental analyses. Complex **1** was also characterized by X-ray crystallography, confirming that copper(II) is coordinated by four nitrogen atoms from two **L**[1] and two oxygen atoms from two perchlorates. Furthermore, all ligands and complexes were tested *in vitro* for their antitumor activities using mouse melanoma cell line B16-F10, HepG2 human hepatoma cell line, and A549 human lung adenocarcinoma cell line. Both complexes displayed potent cytotoxicity and are promising substrates for further investigations.

Keywords: Pyrazole derivative; **C**opper(II) complex; Antitumor activity

1. Introduction

Pyrazole and its derivatives have been widely employed to design coordination polymers due to their importance in medicine, biology, and industry [1–6]. Although many studies have been carried out based on 1,1′-(ethane-1,1-diyl)bis(1H-pyrazole) ligands and their complexes, the focus has been mainly on structure development for topological architectures and physical properties such as photoluminescence, absorbance, framework flexibility, and magnetism [7–12]; only rarely have studies focused on development of chemical and biological applications, such as molecular recognition, antimicrobial, and antitumor activities.

Copper is crucial for life as a fundamental component of metalloproteins and copper(II) complexes have been found with anti-inflammatory [13], anticonvulsant [14], antimicrobial, and antitumor activities [5, 15–17]. Furthermore, copper accumulates in tumors due to selective permeability of cancer cell membranes to copper complexes [18].

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Because of this, a number of copper complexes have been screened for antitumor activity and some were active both *in vivo* and *in vitro* [19, 20].

Therefore, we have synthesized two copper complexes to evaluate them for antitumor properties; **1** and **2** were prepared from newly synthesized bidentate ligands $\mathbf{L^1}$ and $\mathbf{L^2}$. Those ligands and complexes were assayed for antitumor activities against three cancer cell lines (B16-F10 mouse melanoma cell line, HepG2 human hepatoma cell line, and A549 human lung adenocarcinoma cell line) by the MTT method.

2. Experimental

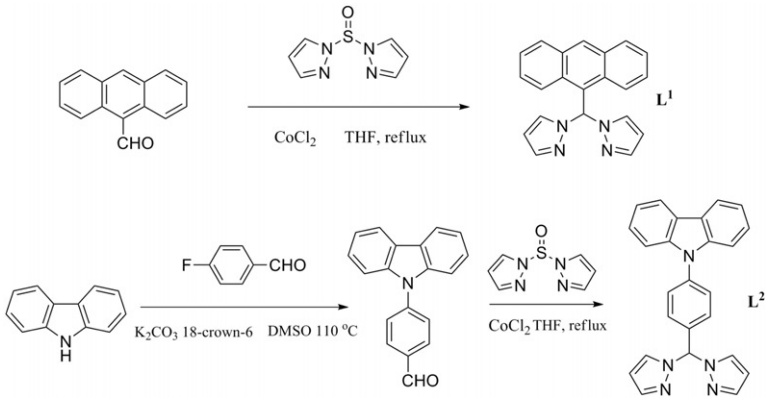
2.1. *Measurements and methods*

All chemicals were of analytical grade. The solvents were purified by conventional methods before use. Elemental analyses were performed with a Perkin-Elmer 240B instrument. Mass spectra were determined with a Micro-mass GCT-MS (EI source). Infrared (IR) spectra were recorded on an NEXUS 870 (Nicolet) spectrophotometer from 4000 cm^{-1} to 400 cm^{-1} with samples prepared as KBr pellets. ^1H NMR spectra were obtained on a Bruker Avance 400 MHz spectrometer (TMS as internal standard). Melting points were recorded with a Perkin–Elmer Pris-1 DMDA-V1 analyzer under N_2 at a heating rate of 5°C min^{-1}.

2.2. *Preparation of L^1, L^2, and their complexes*

2.2.1. Synthesis of 1,1′-(anthracen-9-ylmethylene)bis(1H-pyrazole) ($\mathbf{L^1}$). To a stirred solution of NaH (1.15 g, 48.0 mmol) in THF (50 mL), a solution of pyrazole (3.27 g, 48.0 mmol) was added dropwise at 0°C under nitrogen for 30 min; the solution turned to pale-yellow. Then $SOCl_2$ (2.91 g, 24.0 mmol) was added dropwise at room temperature. Anthracene-9-carbaldehyde (1.00 g, 4.85 mmol) and $CoCl_2$ anhydrous (0.19 g) were added and the reaction mixture was refluxed for 10 h. After cooling to room temperature, water (40 mL) was added and the mixture was stirred for 30 min. The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (3×100 mL). All of the organic fractions were combined and dried over $MgSO_4$. After filtering, most of the filtrate was removed *via* rotary evaporation, leaving an off-white solid which was recrystallized from approximately 80 mL of hot absolute ethanol to afford a white solid. Yield: 0.67 g, 42.6%. IR (KBr, cm^{-1}): 3144 (w), 3111 (w), 3084 (w), 3053 (w), 3006 (w), 1623 (w), 1504 (w), 1447 (m), 1396 (m), 1311 (s), 1295 (s), 1178 (m), 1087 (s), 1039 (s), 964 (m), 911 (m), 849 (m), 813 (s), 771 (s), 757 (s), 732 (s), 609 (m). ^1H NMR (400 MHz, $(CD_3)_2SO$): δ ppm: 6.43–6.44 (t, $J = 2.0$ Hz, 2H), 7.42–7.46 (m, 2H), 7.49–7.53 (m, 2H), 7.56–7.60 (m, $J = 1.2$ Hz, 2H), 7.66 (d, $J = 2.4$ Hz, 2H), 7.99 (d, $J = 9.2$ Hz, 2H), 8.16 (d, $J = 8.4$ Hz, 2H), 8.80 (s, 1H), 9.23 (s, 1H); MS (EI): m/z, 324.14 (scheme 1).

2.2.2. Synthesis of 9-(4-(di(1H-pyrazol-1-yl)methyl)phenyl)-9H-carbazole ($\mathbf{L^2}$). To a stirred solution of NaH (1.15 g, 48.0 m mol) in THF (80 mL), a solution of pyrazole (3.27 g, 48.0 mmol) was added dropwise at 0°C under nitrogen for 30 min, turning the



Scheme 1. The synthetic routes for $\mathbf{L^1}$ and $\mathbf{L^2}$.

solution to a pale-yellow. Then $SOCl_2$ (2.91 g, 24.0 mmol) was added dropwise at room temperature. 4-(9H-carbazol-9-yl)benzaldehyde (1.30 g, 4.8 mmol) and $CoCl_2$ anhydrous (0.24 g) were then added and the reaction mixture was refluxed for 15 h. After cooling to room temperature, water (60 mL) was added and the mixture was stirred for 45 min [21]. The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (4×80 mL). All of the organic fractions were combined and dried over $MgSO_4$. After filtering to remove the drying agent, most of the filtrate was removed *via* rotary evaporation and the residue purified by column chromatography on silica gel with petroleum ether/ethyl acetate (15 : 1) as eluent to give product. Yield: 1.08 g, 57.9%. IR (KBr, cm^{-1}): 3104 (w), 3044 (w), 1600 (s), 1513 (s), 1450 (s), 1225 (s), 1089 (m), 1045 (m), 967 (w), 797 (m), 753 (s), 725 (m), 615 (w). ^1H NMR (400 MHz, $(CD_3)_2SO$): δ ppm: 6.43 (s, 2H), 7.28–7.35 (m, 4H, ArH), 7.42–7.46 (m, 4H), 7.68–7.70 (m, 4H), 7.99–8.00 (d, $J = 1.2$ Hz, 2H), 8.24 (s, 1H), 8.26 (s, 2H); MS (ESI): m/z, 412.15 ($[M + Na]^+$), 801.32 ($[2M + Na]^+$).

2.2.3. Syntheses of complexes 1 and 2 ($\mathbf{L^1}$). (0.11 g, 0.32 mmol) and $Cu(ClO_4)_2 \cdot 6H_2O$ (0.06 g, 0.16 mmol) were dissolved in MeOH (15 mL). The reaction mixture was heated under reflux for 1 h and then allowed to cool to room temperature. The solution was filtered to afford the target complex as green powder 0.12 g (66.04%). Single crystals of **1** were obtained by evaporating slowly in acetonitrile. Anal. Calcd for $C_{42}H_{32}N_8O_8Cl_2Cu$ (%): C, 55.36; H, 3.54: N, 12.30; O, 14.05; Cl, 7.78; Cu, 6.97. Found: C, 55.51; H, 3.53; N, 12.26 %. IR (KBr, cm^{-1}): 3431 (m), 3162 (w), 1625 (w), 1525 (w), 1426 (m), 1310 (m), 1118 (s), 1069 (s), 779 (w), 730 (m), 623 (m).

A similar procedure was also adopted for **2**. Anal. Calcd for $C_{50}H_{38}N_{10}O_8Cl_2Cu$ (%): C, 57.67; H, 3.68; N, 13.45; O, 12.29; Cl, 6.81; Cu, 6.10. Found (%): C, 57.62; H, 3.66; N, 13.50. IR (KBr, cm^{-1}): 3436 (w), 3134 (w), 1602 (m), 1520 (s), 1451 (s), 1232 (m), 1122 (s), 1087 (s), 751 (s), 627 (m), 1122 (s), 1087 (s).

2.3. *Crystal structure determination and refinement*

The crystallographic data for **1** were collected on a Bruker Smart 1000 CCD area detector diffractometer equipped with Mo-Kα ($\lambda = 0.71069$ Å) radiation using the

Table 1. Crystal data and structure refinement for **1**.

Empirical formula	$C_{46}H_{38}N_{10}O_8Cl_2Cu$
Formula weight	993.30
Temperature (K)	298(2)
Wavelength (Å)	0.71069
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions (Å, °)	
a	8.924(2)
b	11.653(3)
c	12.108(3)
α	75.218(4)
β	81.164(4)
γ	70.778(3)
Volume (Å^3), Z	1146.3(5), 1
Calculated density (Mg m^{-3})	1.439
Absorption coefficient (mm^{-1})	1.316
F(000)	511
Crystal size (mm^3)	$0.30 \times 0.30 \times 0.20$
θ range for data collection (°)	1.90–25
Limiting indices	$-10 \le h \le 10$; $-13 \le k \le 13$; $-13 \le l \le 14$
Reflections collected	8058
Independent reflection	3969 [R(int) = 0.0383]
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7787 and 0.6935
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	3969/0/305
Goodness-of-fit on F^2	1.066
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0610$, $wR_2 = 0.1546$
R indices (all data)	$R_1 = 0.0934$, $wR_2 = 0.1760$
Largest difference peak and hole (e Å^{-3})	0.555 and −0.434

ω-scan mode. Empirical absorption correction was applied to the data. Unit cell dimensions were obtained with least-squares refinements and the structure was solved by direct methods with SHELXL-97. All non-hydrogen atoms were located from the trial structure and then refined anisotropically. All hydrogen atoms were generated in idealized positions. All calculations were performed with SHELXL-97 programs [22]. Other relevant parameters of the crystal structure are listed in table 1.

2.4. *Antitumor activity*

The antitumor activities of $\mathbf{L^1}$, $\mathbf{L^2}$, **1**, and **2** against B16-F10, HepG2, and A549 cell lines were evaluated as described elsewhere with some modifications [23]. Target tumor cell lines were grown to log phase in RPMI 1640 medium supplemented with 10% fetal bovine serum. After diluting to 2×10^4 cells mL^{-1} with the complete medium, 100 µL of the obtained cell suspension was added to each well of 96-well culture plates. The subsequent incubation was permitted at 37°C, 5% CO_2 atmosphere for 24 h before the cytotoxicity assessments. Tested samples at pre-set concentrations were added to 6 wells with colchicine and CA-4 coassayed as positive reference. After 48 h exposure period, 40 µL of PBS containing 2.5 mg mL^{-1} of MTT (3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyltetrazolium bromide) was added to each well. Four hours later, 100 µL extraction solution (10% SDS-5% isobutyl alcohol−0.01 mol L^{-1} HCl) was added.

Table 2. IC_{50} values of L^1, L^2, **1**, and **2**.

Compounds	$IC_{50} \pm SD$ ($\mu g\,mL^{-1}$)		
	B16-F10	HepG2	A549
L^1	9.9 ± 1.4	10.1 ± 2.4	8.1 ± 0.9
L^2	11.2 ± 1.9	12.5 ± 2.5	7.8 ± 1.2
1	0.6 ± 0.2	0.8 ± 0.4	0.3 ± 0.1
2	0.9 ± 0.3	1.1 ± 0.3	0.5 ± 0.2
Cisplatin[a]	0.9 ± 0.2	0.7 ± 0.2	1.5 ± 0.1

[a]Data from ref. [26].

Table 3. Selected bond lengths (Å) and angles (°) for **1**.

Cu(1)–N(2)	1.990(3)	N(2)–Cu(1)–N(4)	87.6(1)
Cu(1)–N(4)	2.007(3)	C(19)–N(3)–N(4)	109.6(3)
Cl(1)–O(3)	1.408(4)	C(19)–N(3)–C(15)	130.4(3)
N(3)–C(19)	1.351(5)	N(4)–N(3)–C(15)	119.8(3)
N(3)–N(4)	1.351(4)	C(16)–N(1)–N(2)	109.9(3)
N(3)–C(15)	1.473(5)	C(16)–N(1)–C(15)	130.1(3)
N(1)–C(16)	1.345(5)	N(2)–N(1)–C(15)	119.9(3)
N(1)–N(2)	1.360(4)	N(1)–C(15)–N(3)	109.2(3)
N(1)–C(15)	1.468(4)	N(1)–C(15)–C(14)	113.4(3)
N(4)–C(21)	1.324(5)	N(3)–C(15)–C(14)	112.5(3)
N(2)–C(18)	1.328(5)	C(21–N(4)–N(3)	106.0(3)
C(23)–N(5)	1.096(9)	C(21)–N(4)–Cu(1)	130.0(3)
C(16)–C(17)	1.355(6)	N(3)–N(4)–Cu(1)	123.1(2)
C(19)–C(20)	1.354(6)	C(18)–N(2)–N(1)	105.2(3)
C(15)–C(14)	1.507(5)	C(18)–N(2)–Cu(1)	131.1(3)
C(20)–C(21)	1.381(6)	N(1)–N(2)–Cu(1)	123.6(2)

After an overnight incubation at 37°C, the optical density was measured at 570 nm on an ELISA microplate reader. In all experiments three replicate wells were used for each drug concentration. Each assay was carried out at least three times. The results are summarized in table 2.

3. Results and discussion

3.1. *IR spectrum studies*

For the ligands and copper(II) complexes, $\nu_{(C=N)}$ is a shoulder involving a split sharp peak at 1600–1625 cm^{-1}, while $\nu_{(CH)}$ is a split sharp peak at 3006–3162 cm^{-1}. In Cu(II) complexes, two strong bands are at 1069 and 1118 cm^{-1}; the former can be attributed to $\nu_{(ClO)}$ and the latter to direct coordination of oxygen to copper. These bands shift to higher frequency, *ca* 40–110 cm^{-1}, in the complex, which implies direct coordination of perchlorates to copper, in agreement with X-ray diffraction.

3.2. *Crystal structure of $[CuL^1(CH_3CN)_2](ClO_4)_2$ (1)*

Both complexes show good solubility in methylene chloride and CH_3CN and high solubility in DMF and DMSO. The formation of copper complexes was confirmed by

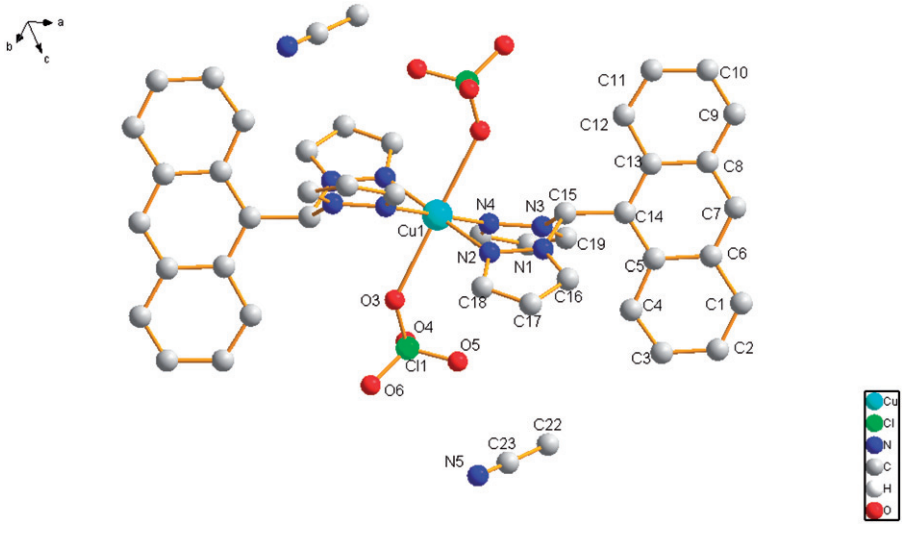


Figure 1. Molecular structure of **1**.

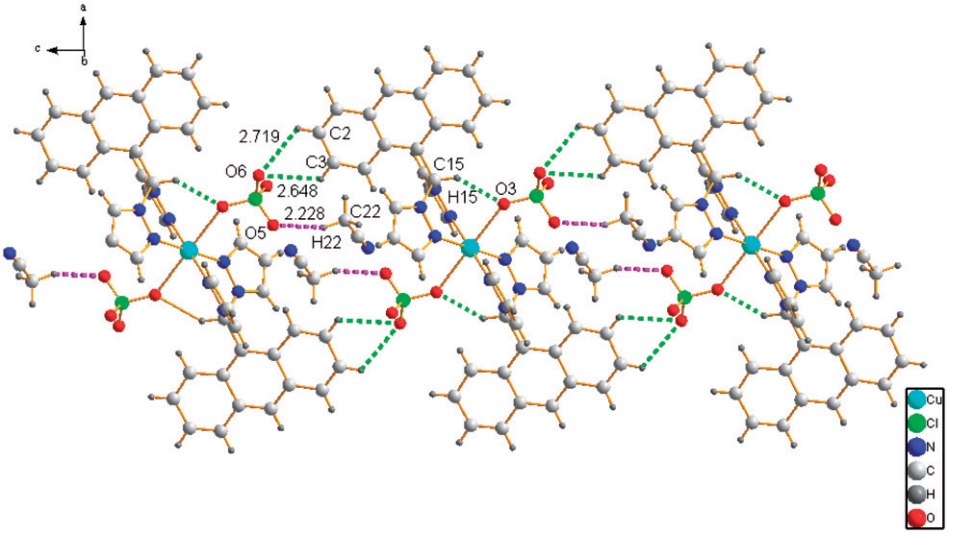


Figure 2. 1-D structure of **1**.

IR and elemental analysis. Single crystals of **1** were obtained by evaporating slowly in acetonitrile.

Complex **1** crystallizes in triclinic with space group P1. Selected bond lengths and angles are listed in table 3. The ORTEP of **1** with atom labeling is shown in figure 1.

As shown in figure 1, the polymer unit consists of a divalent copper, two ligands, two acetonitriles, and two perchlorates. The Cu(II) is N_4-chelated by $\mathbf{L^1}$ and is further coordinated by two perchlorates. The coordination environment of copper is best described as distorted octahedral. An equatorial plane is formed by N2 and N4, axial

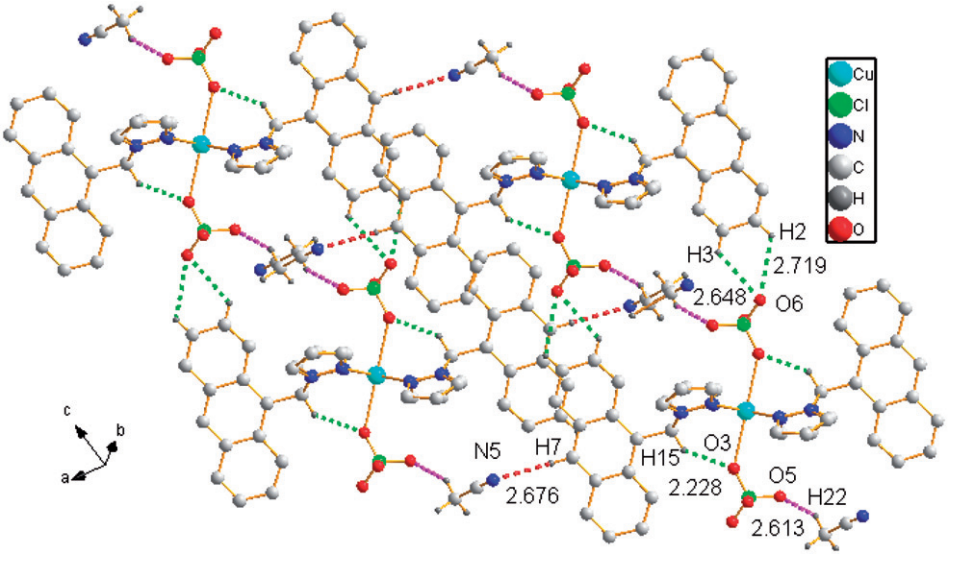


Figure 3. 2-D layer motif of **1**.

position is occupied by perchlorate O5. $[CuL^1(CH_3CN)_2](ClO_4)_2]_n$ units link into polymeric chains, where perchlorates and acetonitriles connect adjacent complexes of the symmetry-related unit in an end-to-end bridging mode, as shown in figures 2 and 3. As shown in figure 2, intermolecular H-bonds (CH···O) formed between adjacent molecules generate a 2-D supramolecular network. The C2H···O6, C3–H···O6 and C22–H···O5 distances are 2.791, 2.6481, and 2.613 Å, respectively.

3.3. *Antitumor activities*

The results of antitumor activities are summarized in table 2. The IC_{50} values are expressed in microgram per milliliter, together with that of cisplatin for comparison. Free ligands show no significant growth inhibition activities, indicating that chelation of $\mathbf{L^1}$ and $\mathbf{L^2}$ with copper was essential for antitumor activities. Antitumor studies on the A549 human lung adenocarcinoma cell line show that **1** and **2** are potent cytotoxic with IC_{50} values of $0.3 \pm 0.1\,\mu g\,mL^{-1}$ and $0.5 \pm 0.2\,\mu g\,mL^{-1}$, which are better than cisplatin ($1.5 \pm 0.1\,\mu g\,mL^{-1}$). The enhanced antitumor activity on complexation with copper(II) may be explained by chelation [15, 24, 25]. Further work is in progress to elucidate the detailed mechanisms of antitumor activity of the copper(II) complexes.

Supplementary material

Crystallographic data for the structure reported in this article have been deposited with the Cambridge Crystallographic Data Center, CCDC reference number 831560. Copies of these information may be obtained free of charge from: The Director,

CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336033; E-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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