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Dedicated to Academician N.T. Kuznetsov on the occasion of his 90th birthday

Influence of Trifluoromethyl Groups on the Crystal Packing of the Binuclear Copper(II) Complex Based on N_2O_3-Pentadentate (Hydroxy)bis(CF_3-enaminoketone)

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Abstract—The reaction of 1,1,1-trifluoro-4-methoxy-3-penten-2-one (L^1) with 1,3-diaminopropan-2-ol affords *N*,*N*'-(2-hydroxypropane-1,3-diyl)bis(trifluoroacetylacetimine) (H_3L^2) in a yield of 82%. In the absence of additional bases, the synthesized N_2O_3 ligand reacts with copper(II) acetate to give the binuclear complex $[Cu_2L^2(OAc)]$ (**I**), the structure of which is determined by X-ray structure analysis (CIF file CCDC no. 2071133).

Keywords: enaminoketones, Schiff bases, binuclear copper(II) bases, X-ray structure analysis
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INTRODUCTION

Binuclear copper(II) complexes remain to be among attractive objects for investigation during several decades. On the one hand, the Cu(II) complexes with bridging μ-phenoxy, μ-alkoxy, or μ-hydroxy groups forming the binuclear metallic cage are model systems for studying spin–spin exchange interactions between two lone electrons [1–5]. On the other hand, the cytotoxic effect against human cancer cells exhibited by the Cu(II) complexes forms a basis for the target design of the ligand capable of selective binding and further cleaving harmful DNA, which diminishes the development of tumors [6]. The studies of the Cu_2 complexes in various catalytic systems are also very important, since they represent a substantiated alternative for the used catalysts based on the Platinum Group metals from the economic and environmental points of view [7–9].

The Schiff bases are often used as ligands for the building of the binuclear cage with copper(II) atoms [1, 10–16]. Enaminoketones containing additional donor atoms extend the series of polydentate compounds, resulting in the formation of the mono- and polynuclear copper(II) complexes, depending on the synthesis conditions [17–23].

The introduction of fluorine-containing substituents in the ligand structure plays an important role in the self-organization of molecules, including the crystallization of the metal complexes [24–26]. In addition to the well-known intermolecular interactions (hydrogen bonds, π–π stacking, and C–H...π), increasing attention is given to weak contacts (such as C–F...H, F...F, or C–F...π) determining the structure and properties of the crystals [26].

In this work, we synthesized the binuclear copper(II) complex $[Cu_2L^2(OAc)]$ (**I**) on the basis of new fluorine-containing functionalized enaminoketone (H_3L^2) under mild conditions and studied specific features of its crystal structure.

EXPERIMENTAL

All procedures associated with the synthesis of ligand H_3L^2 and complex **I** were carried out in air using commercially available reagents: $Cu(OAc)_2 \cdot H_2O$ (analytical grade, Vekton), 1,3-diaminopropan-2-ol (99%, Alfa Aesar), diethyl ether (analytical grade, Vekton), acetonitrile (analytical grade, Vekton), and methanol (reagent grade, Vekton). Trifluoromethyl-containing alkoxyenone (L^1) was synthesized using a known procedure [27] from 2-methoxypropene and

trifluoroacetic anhydride in the presence of pyridine in dichloromethane.

^1H, ^{19}F, and ^{13}C NMR spectra were recorded on a Bruker DRX-500 spectrometer (500 MHz) with Me_4Si and C_6F_6 as internal standards. The IR spectra of the compounds were recorded on a PerkinElmer Spectrum One FT-IR spectrometer in a range of 400–4000 cm^{-1} using a diffuse reflectance accessory for solid substances. Elemental analysis was carried out on a PerkinElmer PE 2400 Series II automated analyzer.

Synthesis of *N*,*N*'-(2-hydroxypropane-1,3-diyl)bis-(trifluoroacetylacetimine) (H_3L^2). Alkoxyenone L^1 (1.53 g, 9 mmol) was added dropwise to a solution (cooled to 0°C) of 1,3-diaminopropan-2-ol (0.41 g, 4.5 mmol) in diethyl ether (25 mL). The reaction mixture was stirred until a white precipitate was formed, which was filtered off and dried in air. The yield was 1.35 g (82%). White powder, T_m = 142–144°C.

For $C_{13}H_{16}N_2O_3F_6$			
Anal. calcd., %	C, 43.10	H, 4.45	N, 7.73
Found, %	C, 42.96	H, 4.32	N, 7.54

IR (ν, cm^{-1}): 3304, 3135 (O–H), 2949, 2929 ν(C–H), 1616 (C=O), 1577 (C=C), 1441 $\nu_{as}(CH_3)$, 1250, 1188, 1137 ν(C–F). ^1H NMR (500 MHz, CD_3CN), δ, ppm: 2.11 (s, 6H, 2 CH_3), 3.39 (m, 2H, CH_2), 3.52 (m, 2H, CH_2), 3.96 (tt, 1H, J_{HH} = 7.7, 3.7 Hz, C<u>H</u>OH), 5.38 (s, 2H, 2 CH=), 11.20 (s, 2H, NH). ^{19}F NMR (470 MHz, CD_3CN), δ, ppm: 87.29 (s, CF_3). ^{13}C NMR (125 MHz, CD_3CN), δ, ppm: 19.95 (s, CH_3), 47.96 (s, CH_2NH), 69.40 (s, CHOH), 89.94 (s, <u>C</u>CH_3), 119.0 (q, $^2J_{CF}$ = 288 Hz, CF_3), 172.38 (s, <u>C</u>HCO), 175.12 (q, $^3J_{CF}$ = 32 Hz, C=O).

Synthesis of complex [$Cu_2L(OAc)$] (I). Compound $Cu(OAc)_2 \cdot H_2O$ (139 mg, 0.7 mmol) was added to compound H_3L^2 (128 mg, 0.35 mmol) in methanol (10 mL), the mixture was stirred at room temperature for 1 h, and water (50 mL) was poured. The formed precipitate was filtered off and dried. Then the obtained complex was dissolved in acetonitrile and passed through the Celite® 545 layer. The slow evaporation of the solvent resulted in the formation of blue crystals of complex **I**. T_m = 303–304°C. The yield was 183 mg (93%).

For $C_{15}H_{16}N_2O_5F_6Cu_2$			
Anal. calcd., %	C, 33.03	H, 2.96	N, 5.14
Found, %	C, 32.83	H, 2.73	N, 5.10

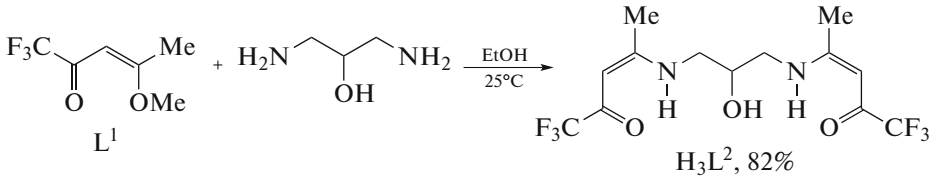
IR (ν, cm^{-1}): 2952, 2841 ν(C–H), 1625 ν(C=O), 1568 (C=C), 1479, 1466 $\nu_{as}(CH_3)$, 1248–1149 ν(C–F).

X-ray structure analysis (XSA). The crystallographic data for a single crystal of complex **I** were obtained on an Xcalibur 3 automated four-circle diffractormeter with a CCD detector using a standard procedure (MoK_α radiation, graphite monochromator, ω scan mode with an increment of 1° at 295(2) K). An empirical absorption correction was applied. The structure was determined by a direct statistical method and refined by full-matrix least squares for F^2 in the anisotropic approximation for all non-hydrogen atoms. Hydrogen atoms were placed in the geometrically calculated positions and refined by the riding model. All calculations were performed in the Olex program shell [28] using the SHELX program package [29].

The atomic coordinates and other structural parameters of compound **I** were deposited with the Cambridge Crystallographic Data Centre (CIF file CCDC no. 2071133; deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk/data_request/cif).

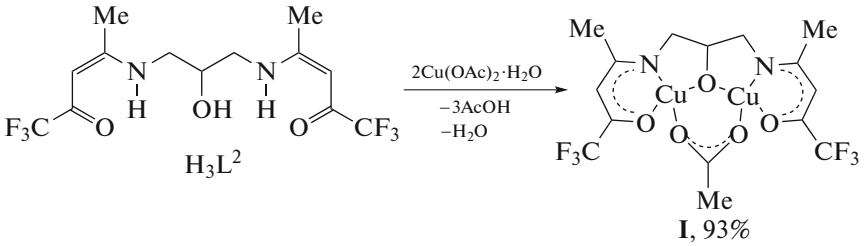
RESULTS AND DISCUSSION

The reaction of alkoxyenone L^1 with diaminopropanol in a ratio of 2 : 1 in ether on cooling gave for the first time bis(CF_3-enaminoketone) H_3L^2 containing two *N*,*O*-enaminoketone moieties capable of chelating and additional hydroxyl group that forms two tridentate NO_2 fragments (Scheme 1). The structure of ligand H_3L^2 was confirmed by the data of NMR and IR spectroscopy and elemental analysis. The ^1H NMR spectrum of compound H_3L^2 in a CD_3CN solution exhibits singlets at 2.11, 5.36, and 11.20 ppm assigned to the enaminoketone moiety, namely, to the methyl substituent, methine proton, and N–H group, respectively. Multiplets of the diaminopropanol moiety are detected at δ_H = 3.39, 3.52, and 3.96 ppm. The ^{19}F NMR spectrum contains a singlet of the trifluoromethyl group at δ_F = 87.3 ppm lying in the range characteristic of the trifluoroacetyl-containing compounds [18–22]. One set of signals from carbon of ligand H_3L^2 is also detected in the ^{13}C NMR spectrum. Thus, in a CD_3CN solution both enaminoketone moieties of compound H_3L^2 exist in the most favorable *Z*,*Z* form, most likely, due to intramolecular hydrogen bonds.



Scheme 1.

The "cubane" structure $[(Cu(HL^3))_4]$ has previously been synthesized by the reaction of the non-fluorinated analogue of H_3L^2 (*N*,*N*'-(2-hydroxypropane-1,3-diyl)-bis(acetylacetimine) (H_3L^3)) with copper(II) perchlorate in the presence of trimethylamine [30]. Under similar conditions, attempts to isolate the products of the reactions of H_3L^2 with the divalent copper salts were unsuccessful. However, in the absence of nitrous bases, the reaction of (hydroxyl)bis(CF_3-enaminoketone) H_3L^2 with copper(II) acetate afforded complex **I** in a high yield (Scheme 2). Thus, acetate anions act as a mild base for the deprotonation of ligand H_3L^2. The slow evaporation of an acetonitrile solution of compound **I** gives the crystals suitable for XSA (Fig. 1).



Scheme 2.

According to the XSA data, the neutral binuclear copper(II) complex (**I**) crystallizes in the $P2_1/c$ space group of the monoclinic system (Fig. 1, Table 1). The planar square coordination environment of two copper(II) atoms is formed due to the involvement of the enaminoketone moieties, μ-hydroxy group of ligand H_3L^2, and μ-bridging acetate anion. Three different metallocycles are formed around each copper atom: the six- and five-membered rings with two different heteroatoms (A and B, Fig. 1) and the six-membered ring with three oxygen atoms containing two metal atoms (C, Fig. 1). The planes of two chelate enaminoketone moieties are characterized by an insignificant deviation with a dihedral angle of 6.6(4)°. The distance between the copper atoms in complex **I** is 3.481(1) Å, which is comparable with one of the values (3.438(1) Å) for Cu...Cu in the $[(Cu(HL^3))_4]$ cluster based on the non-fluorinated analogue H_3L^3 [30].

The introduction of the trifluoromethyl group in the enaminoketone moiety results in the formation of the intramolecular short contact between the fluorine atom and methine hydrogen atom equal to 2.49(7) Å. The molecules of complex **I** form pseudodimeric structures with an interplanar distance of ~3.4 Å (the planes passing through the N(1)O(1)N(2)O(1) atoms of the molecules). Two intermolecular contacts F...H between the CF_3 and CH_3 groups equal to 2.517(5) Å (Fig. 2) are symmetrically accomplished in the pseudodimers. The O(3) and O(3)' oxygen atoms of the bridging alkoxide groups shift from the plane of the molecules by 0.267 Å, which results in the shorter contacts Cu(2)–O(3)' and Cu(2)'–O(3) equal to 3.108(6) Å with the shortest intermolecular distance between the copper atoms Cu(2)–Cu(2)' equal to 3.778(1) Å (Fig. 2).

The pseudodimers form piles due to the F...H contacts between the fluorine atoms and H(7) and H(13) atoms of the alkoxide and methyl groups of complex **I** (Fig. 3).

It is shown in this work that functionalized fluorine-containing enaminoketone easily enters into complex formation with copper(II) acetate. Unlike the non-fluorinated analogues, no basic agents, including trimethylamine, are needed for this reaction to occur. The pentadentate ligand participates in the formation of the binuclear copper(II) complex, and one acetate anion is retained as the bridging coligand. The trifluoromethyl groups were found to form short intra- and intermolecular F...H contacts with the formation of the crystal structure of the complex, a specific feature of which is the formation of pseudodimers.

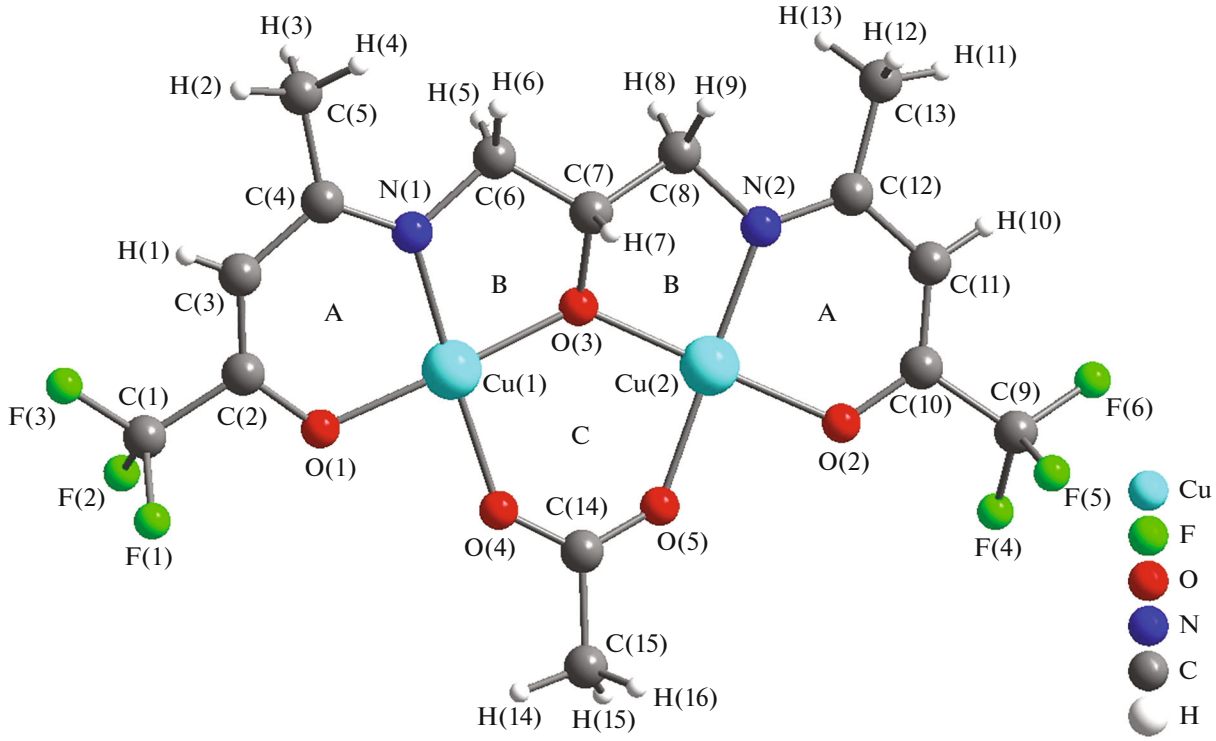


Fig. 1. Molecular structure of complex **I**.

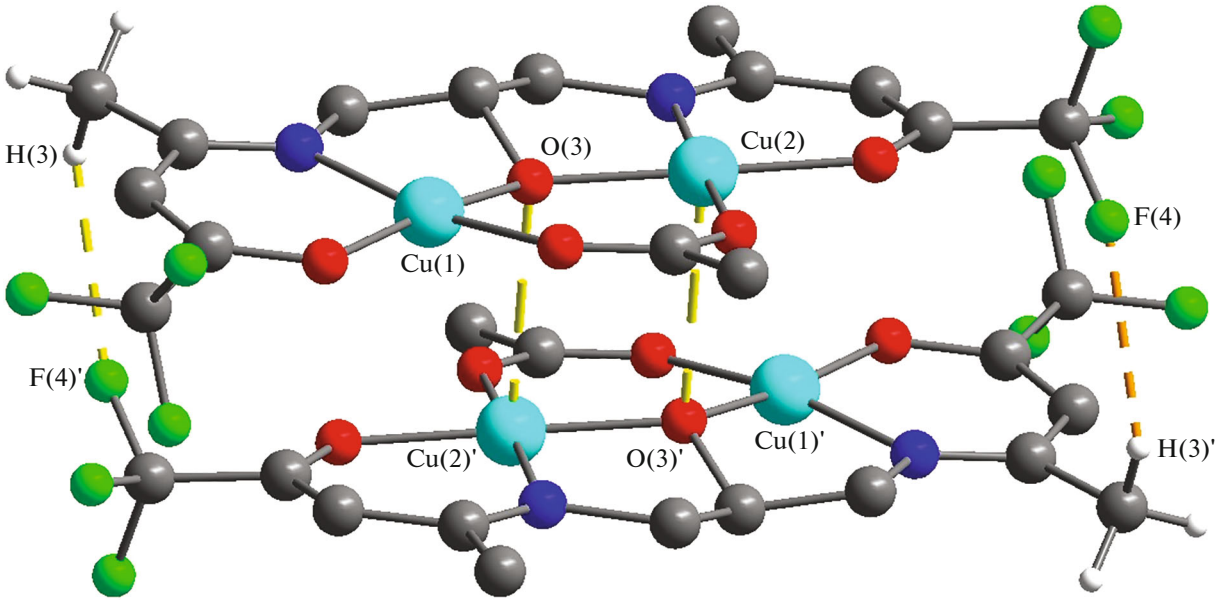


Fig. 2. Pseudodimer of complex **I**. Hydrogen atoms are partially omitted. The intermolecular contacts F(4)...H(3)' and F(4)'...H(3) are 2.517(5) Å, the Cu(2)...O(3)' and Cu(2)'...O(3) distances are 3.108(6) Å, and Cu(1)...Cu(1)' is 6.391(1) Å.

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Table 1. Selected crystallographic characteristics and parameters of the XSA experiment for complex **I**

Parameter	Value
Empirical formula	$C_{15}H_{16}N_2O_5F_6Cu_2$
FW	545.38
Crystal system	Monoclinic
Space group	$P2_1/c$
a, Å	10.834(1)
b, Å	11.519(1)
c, Å	15.284(3)
α, deg	90.00
β, deg	101.99(2)
γ, deg	90.00
V, Å^3	1865.8(5)
Z	4
ρ_{calc}, g cm^{-3}	1.942
μ, mm^{-1}	2.3708
Crystal size, mm	0.39 × 0.19 × 0.08
θ_{min}–θ_{max}, deg	3.76–26.21
F(000)	1088
R_{int}	0.0905
Ranges of reflection indices	$-13 \le h \le 10$, $-14 \le k \le 14$, $-18 \le l \le 19$
Measured reflections	12134
Independent reflections	3803
Number of reflections with $I > 2\sigma(I)$	2238
GOOF	1.000
R factors for $F^2 > 2\sigma(F^2)$	$R_1 = 0.0600$, $wR_2 = 0.1387$
R factors for all reflections	$R_1 = 0.1136$, $wR_2 = 0.1802$
Residual electron density (max/min), e/Å^3	0.61/–0.68

Table 2. Selected bond lengths and bond angles in complex **I**

Bond	*d*, Å	Angle	ω, deg
Cu(1)–O(1)	1.898(5)	O(1)Cu(1)N(1)	94.70(20)
Cu(1)–N(1)	1.939(6)	N(1)Cu(1)O(3)	85.06(19)
Cu(1)–O(4)	1.929(5)	O(1)Cu(1)O(4)	85.67(20)
Cu(1)–O(3)	1.918(4)	O(3)Cu(1)O(4)	95.83(19)
Cu(2)–O(2)	1.910(5)	O(2)Cu(2)N(2)	93.98(22)
Cu(2)–N(2)	1.931(5)	N(2)Cu(2)O(3)	85.22(20)
Cu(2)–O(5)	1.932(5)	O(2)Cu(2)O(5)	86.08(20)
Cu(2)–O(3)	1.912(5)	O(3)Cu(2)O(5)	94.68(18)
		Cu(1)O(3)Cu(2)	130.67(22)

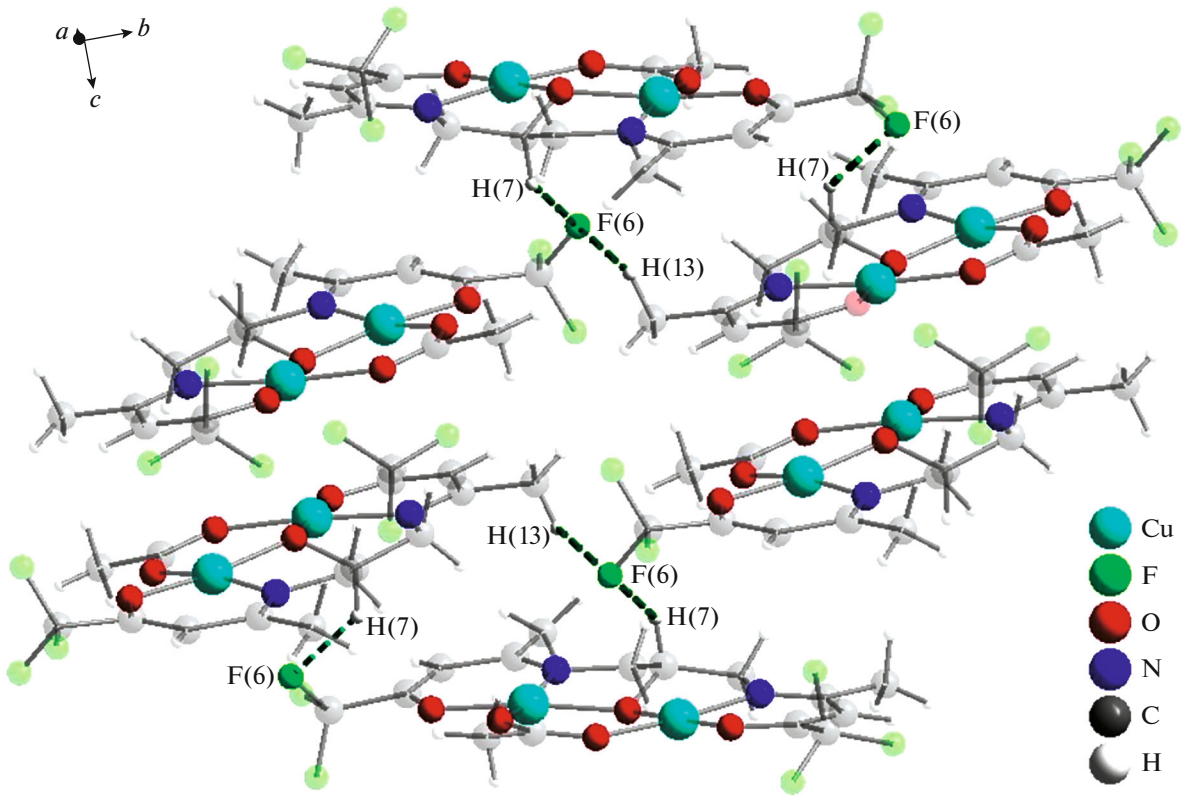

Fig. 3. Intermolecular interactions F...H in complex **I**. The F(6)...H(13) and F(6)...H(7) distances are 2.968(6) and 2.726(5) Å, respectively.

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CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

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