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The synthesis and crystal and molecular structure of *mer*-tris(3-trimethylsilyl-2-pyridinethiolato)cobalt(III)

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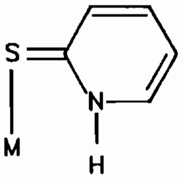
Abstract

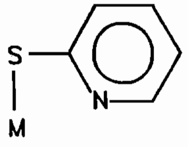
The room temperature reaction of $[Co(H_2O)_6]Cl_2$ with 3-trimethylsilyl-2-pyridinethiol in methanol yields $[Co(2\text{-}SC_5H_3N\text{-}3\text{-}SiMe_3)_3]$. The crystal structure determination revealed the meridional ligand arrangement, as previously reported for the analogous $[Co(2\text{-}SC_5H_4N]$. Crystal data: $C_{24}H_{36}N_3Si_3S_3Co$, monoclinic space group $P2_1/c$, $a=9.416(2)$, $b=29.163(4)$, $c=12.371(2)$ Å. $\beta=106.81(1)°$, $Z=4$, $D_{calc}=1.23$ g cm^{-3}; structure solution and refinement based on 1032 reflections with $F_o \geq 6\sigma(F_o)$ (Mo Kα, $\lambda=0.71073$ Å) converged at $R=0.069$.

Introduction

The pyridine-2-thione ligand displays unusual versatility in coordinating to metal centers. The ligand often adopts the neutral 1H-pyridine-2-thione form (**A**) [1–7]. As the conjugate anion, pyridine-2-thiolate, the ligand is commonly monodentate through the S donor (**B**) [8, 9], or bidentate through the S and N donors (**C**) [10–16], although bridging modes through both heteroatoms (**D**) [17–21] or exclusively through the thiolate donor (**E**) [22] may be adopted.



A



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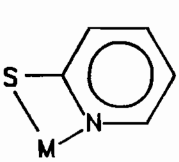

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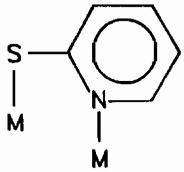

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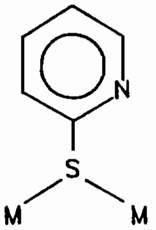
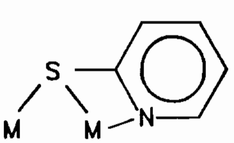
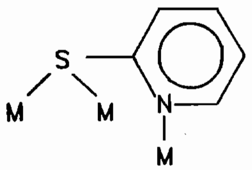


E

In addition, the ligand may function as a five-electron donor in the μ_3 modes (**F**) [23] and (**G**) [24].



F



G

In an effort to modify the microenvironment about a metal center coordinated to this ligand type by introducing varying degrees of steric constraints, we have synthesized a series of novel 3-(triorganosilyl)pyridine-2-thiols (**H**) and 3,6-bis(triorganosilyl)pyridine-2-thiols (**I**) and described their coordination chemistry with Ag(I), Cu(I), Hg(II) and Mo(III)–Mo(V) [25–35].

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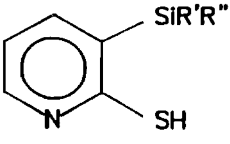
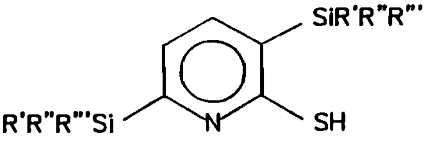


H



I

As part of our investigations of the properties of these ligands, we have prepared several Co(III) complexes and structurally characterized the 3-(triorganosilyl)pyridine-2-thiol derivative $[Co(2\text{-}SC_5H_3N\text{-}3\text{-}SiMe_3)_3]$. The structure of the complex $[Co(2\text{-}SC_5H_4N)_3]$ containing the unsubstituted 2-pyridinethiol ligand was also determined in order to allow an assessment of the structural consequences of the presence of the bulky substituents. While this manuscript was in preparation, an independent description of the structure of $[Co(2\text{-}SC_5H_4N)_3$ appeared [36].

Experimental

The ligands $2\text{-}HSC_5H_3N\text{-}3\text{-}SiMe_3$, $2\text{-}HSC_5H_3N\text{-}6\text{-}SiMe_2Bu^t$ and $2\text{-}HSC_5H_2N\text{-}3,6\text{-}(SiMe_2Bu^t)_2$ were prepared as previously described [32]. Dichloromethane was technical grade and was distilled from $CoCl_2$ and P_4O_{10}. The following instruments were used in the study: IR, Perkin-Elmer 283 B IR spectrophotometer, X-ray crystallography, Rigaku AFC-5S four-circle diffractometer; electrochemistry, BAS electroanalytical system.

Synthesis of $[Co(2\text{-}SC_5H_4N)_3]$

To a suspension of $[Co(acac)_3]$ (0.428 g, 1.0 mmol) in methanol (20 ml) was added a solution of 2-pyridinethiol (0.333 g, 3.0 mmol) and triethylamine (0.303 g, 3.0 mmol) in methanol (10 ml). After stirring for 2 h, the brown reaction mixture was evaporated to dryness *in vacuo*. The brown solid was dissolved in CH_2Cl_2 (10 ml), and the resultant dark brown solution was carefully layered with diethyl ether (10 ml). After standing for 5 days at 4 °C, lustrous brown crystals of $[Co(SC_5H_4N)_3]$ deposited on the sides of the crystallization flask. *Anal.* Calc. for $C_{15}H_{12}N_3S_3Co$: C, 46.3; H, 3.02; N, 10.8; Found: C, 46.2; H, 3.06; N, 10.7%.

Synthesis of $[Co(2\text{-}SC_5H_3N\text{-}3\text{-}SiMe_3)_3]$

A solution of $[Co(H_2O)_6]Cl_2$ (0.238 g, 1.0 mmol) in methanol (10 ml) was treated in air with $2\text{-}HSC_5H_3N\text{-}3\text{-}SiMe_3$ (0.549 g, 3.0 mmol) in methanol (5 ml). After stirring for 3 h, the solution was concentrated to 10 ml and layered with diethyl ether (15 ml). Brown crystals were collected after 7 days in 72% yield. *Anal.* Calc. for $C_{24}H_{36}N_3Si_3S_3Co$: C, 47.6; H, 5.95; N, 6.94. Found: C, 47.5; H, 5.90; N, 6.88%.

The complexes $[Co(2\text{-}SC_5H_3N\text{-}3\text{-}SiMe_2Bu^t)_3]$ and $[Co\{2\text{-}SC_5H_2N\text{-}3,6\text{-}(SiMe_2Bu^t)_2\}_3]$ were prepared analogously.

Electrochemical studies

Cyclic voltammetry was performed on solutions 1×10^{-3} M in complex in methylene chloride solution 0.1 M in $(n\text{-}C_4H_9)_4NPF_6$ as supporting electrolyte at a platinum bead working electrode. Controlled potential electrolyses were studied at a platinum gauge electrode employing a conventional isolated three-electrode configuration.

X-ray structure determinations

Full details of the crystallographic methodologies may be found in ref. 37. The crystal data and experimental conditions are summarized in Table 1.

In no instance was an extinction correction applied to the data. Idealized hydrogen atom positions were used throughout the analysis, with the C–H distances set at 0.96 Å. All non-hydrogen atoms of $[Co(2\text{-}SC_5H_4N)_3]$ were refined anisotropically. Only the cobalt, sulfur and silicon atoms of $[Co(2\text{-}SC_5H_3N\text{-}SiMe_3)_3]$ were refined anisotropically.

Results and discussion

The introduction of triorganosilyl substituents into the 2-pyridinethiol group affords a number of advantages over the unsubstituted ligand, among these an enhanced solubility of the metal complexes, the ability to control oligomerization processes by tuning the steric bulk of the substituent, and the tendency of the sterically encumbered ligand to stabilize the higher oxidation states of the metal with respect to the auto-redox reaction [38]. This latter observation seems counterintuitive, since a bulkier ligand would be expected to result in longer metal–donor distances and hence to favor the lower oxidation state. However, the stabilization of higher oxidation states by sterically-hindered thiolates is well documented [38, 40].

The reactions of $2\text{-}HSC_5H_4N$ with Co(II) precursors under anaerobic conditions yielded complexes of the types $[Co(SC_5H_4NH)_2Cl_2]$ and $[Co(SC_5H_4NH)_4](NO_3)_2$, in which the ligand adopts the

TABLE 1. Summary of crystal data and experimental conditions for the X-ray studies

Crystal data		
Empirical formula	$C_{24}H_{36}N_3Si_3S_3Co$	$C_{15}H_{12}N_3S_3Co$
Color, habit	brown parallelepiped	brown needle
Crystal size (mm)	0.21 × 0.19 × 0.23	0.24 × 0.35 × 0.23
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$	$C2/c$
Unit cell dimensions		
a (Å)	9.416(2)	26.687(3)
b (Å)	29.163(4)	9.343(2)
c (Å)	12.372(2)	13.430(4)
β (°)	106.81(1)	100.73(1)
Volume (Å^3)	3262.7(10)	3290.7(11)
Z	4	8
Formula weight	606.0	389.4
Density (calc.) (g cm^{-3})	1.23	1.57
Density (exp.) (g cm^{-3})	1.21(1)	1.55(1)
Absorption coefficient (cm^{-1})	8.34	14.04
$F(000)$	1272.0	1584.0
Data collection		
Diffractometer	Rigaku AFC5S	
Radiation	Mo Kα ($\lambda = 0.71073$ Å)	
Temperature (K)	296	
Monochromator	highly oriented graphite crystal	
2θ range (°)	2.5–45.0	
Scan speed (°/min)	2–6	
Scan range	1.20° plus Kα separation	
Background measurement	stationary crystal and stationary counter at the beginning and end of each scan	
Standard reflections	3 measured every 200 reflections	
Index ranges	$0 \leqslant h \leqslant 10$, $0 \leqslant h \leqslant 28$, $0 \leqslant k \leqslant 30$, $0 \leqslant k \leqslant 12$, $-11 \leqslant l \leqslant 1$, $-17 \leqslant l \leqslant 14$	
Reflections collected	2981	2873
Observed reflections	1032 $(F_o \geqslant 6\sigma(F_o))$	1473 $(F_o \leqslant 6\sigma(F_o)]$
Absorption correction	based on Ψ-scans for 5 reflections with χ near 90° or 270°	
Solution and refinement		
System used	MSC TEXSAN solution package	
Solution	Patterson method	
Refinement method	full-matrix least-squares	
Quantity minimized	$\Sigma w(F_o - F_c)^2$	
Hydrogen atoms	riding model	
Weighting scheme	$w^{-1} = \sigma(F) + 0.0011F^2$	
Final R indices (obs. data) R	0.069	0.052
R_w	0.073	0.058
Goodness of fit	1.78	1.71
Largest and mean Δ/σ	0.007, 0.001	0.005, 0.002
Data to parameter ratio	6:1	7:1
Largest difference peak (e Å^{-3})	0.45	0.23
Largest difference hole	0.53	0.17

neutral thione form. Similar observations had been reported previously [1, 2, 39]. The Co(III) thiolate complex $[Co(SC_5H_4N)_3]$ was produced only in the presence of an oxidant and then only after prolonged refluxing. In contrast, the room temperature reaction of $[Co(H_2O)_6]Cl_2$ with the sterically encumbered 2-HSC_5H_3N-3-$SiMe_3$ in methanol in the presence of atmospheric oxygen rapidly yielded the oxidized product $[Co(2\text{-}SC_5H_3N\text{-}3\text{-}SiMe_3)_3]$ in good yield. The stabilization of the Co(III) oxidation state by the sterically encumbered ligand is also evident in the electrochemical behavior of the complexes. Whereas $[Co(2\text{-}SC_5H_4N)_3]$ exhibits a single quasi-reversible reduction at −0.56 V in the cyclic voltammogram, the irreversible reduction process of $[Co(2\text{-}SC_5H_3N\text{-}3\text{-}SiMe_3)_3]$ is centered at −0.76 V under similar

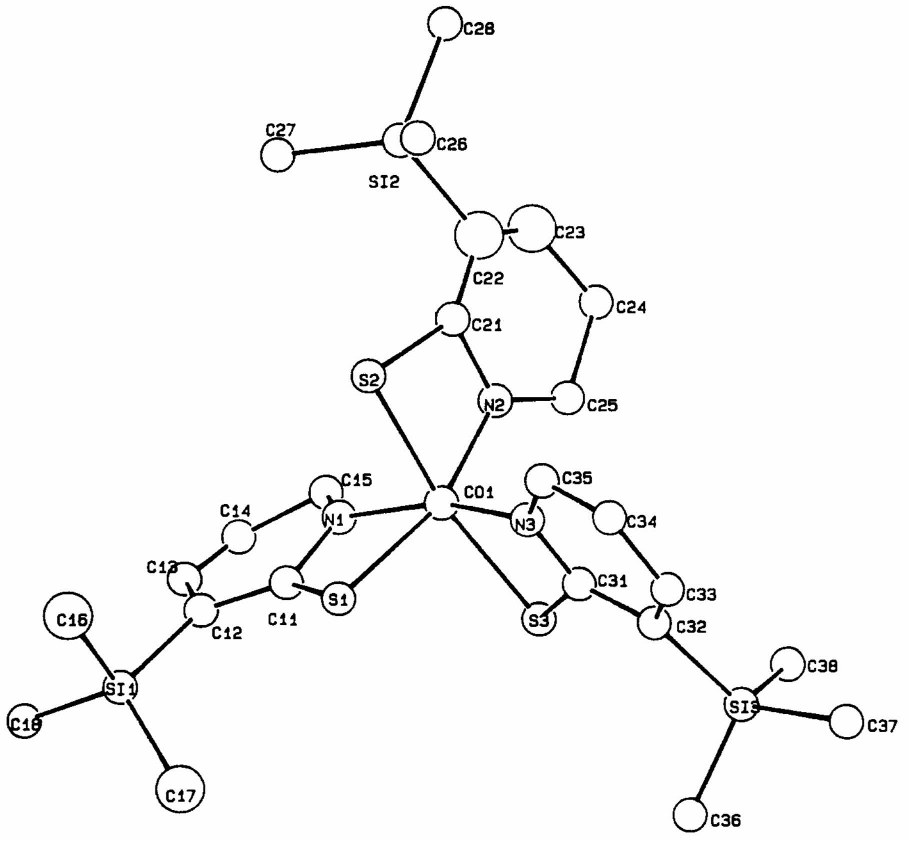


Fig. 1. ORTEP view of the structure of [Co(2-SC_5H_3N-3-$SiMe_3$)] showing the atom-labelling sche

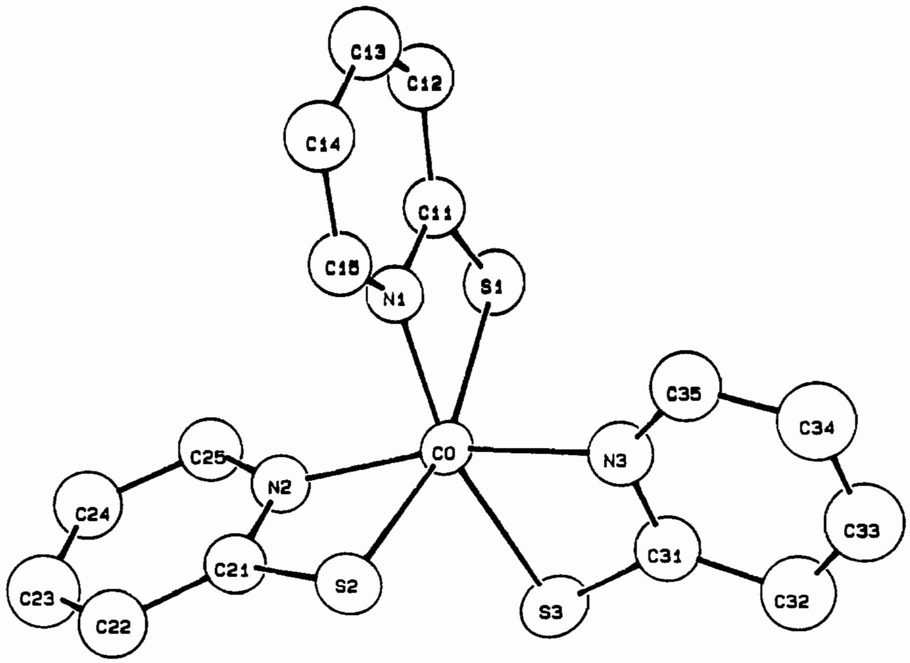


Fig. 2. ORTEP view of the structure of [Co(2-SC_5H_4N)$_3$] showing the atom-labelling scheme.

TABLE 2. Positional parameters for [Co(2-SC_5H_3N-3-$SiMe_3$)$_3$]

Atom	x	y	z
Co(1)	0.5216(4)	0.1295(1)	0.6126(3)
S(1)	0.2835(8)	0.1195(3)	0.5178(7)
S(2)	0.5739(8)	0.1854(2)	0.4997(6)
S(3)	0.5154(9)	0.0834(2)	0.7636(7)
Si(1)	0.1061(9)	0.0540(3)	0.2817(7)
Si(2)	0.9031(9)	0.2352(3)	0.4775(7)
Si(3)	0.455(1)	0.1107(3)	1.0261(8)
N(1)	0.514(2)	0.0836(7)	0.502(2)
N(2)	0.729(2)	0.1400(7)	0.654(2)
N(3)	0.482(2)	0.1661(8)	0.723(2)
C(11)	0.369(3)	0.0807(8)	0.446(2)
C(12)	0.306(2)	0.0530(7)	0.355(2)
C(13)	0.407(3)	0.027(1)	0.325(2)
C(14)	0.559(3)	0.028(1)	0.378(2)
C(15)	0.611(3)	0.056(1)	0.467(2)
C(16)	0.060(3)	0.107(1)	0.211(3)
C(17)	−0.005(4)	0.045(1)	0.378(3)
C(18)	0.063(3)	0.010(1)	0.175(3)
C(21)	0.748(3)	0.172(1)	0.586(2)
C(22)	0.884(3)	0.1909(9)	0.579(2)
C(23)	1.011(3)	0.171(1)	0.666(3)
C(24)	0.988(3)	0.138(1)	0.738(2)
C(25)	0.849(3)	0.125(1)	0.731(1)
C(26)	0.814(3)	0.2898(9)	0.502(2)
C(27)	0.821(3)	0.214(1)	0.335(3)
C(28)	1.101(3)	0.246(1)	0.498(3)
C(31)	0.477(3)	0.1371(9)	0.808(2)
C(32)	0.442(2)	0.1511(8)	0.905(2)
C(33)	0.406(3)	0.198(1)	0.908(2)
C(34)	0.401(2)	0.2271(8)	0.822(2)
C(35)	0.444(3)	0.214(1)	0.732(2)
C(36)	0.310(3)	0.067(1)	0.984(2)
C(37)	0.430(3)	0.143(1)	1.142(3)
C(38)	0.636(3)	0.085(1)	1.069(2)

conditions (acetonitrile, [$(C_4H_9)_4N$][PF_6] supporting electrolyte, ferrocene/ferrocenium internal couple).

The molecular structure of [Co(2-SC_5H_3N-3-$SiMe_3$)$_3$] is shown in Fig. 1 and that of [Co(2-SC_5H_4N)$_3$] in Fig. 2. Atomic positional parameters are listed in Tables 2 and 3 for [Co(2-SC_5H_3N-3-$SiMe_3$)$_3$] and [Co(2-SC_5H_4N)$_3$], respectively. Bond lengths and angles are compared in Table 4. The cobalt center of [Co(2-SC_5H_3N-3-$SiMe_3$)$_3$] displays the meridional arrangement of the ligands, as previously reported for the analogous [Co(2-SC_5H_4N)$_3$] and [Rh(2-SC_5H_4N)$_3$] [3]. The comparison of the bonding parameters of [Co(2-SC_5H_3N-3-$SiMe_3$)$_3$] and [Co(2-SC_5H_4N)$_3$] in Table 4 suggests that the triorganosilyl groups do not grossly influence the structural features associated with the [CoS_3N_3] core. This observation is consistent with our detailed investigations of the structures of 3-triorganosilyl-2-pyridinethiols and 3,6-bistriorganosilyl-2-pyridinethiols which illustrate that significantly bulkier groups than

TABLE 3. Positional parameters for [Co(2-SC_5H_4N)$_3$]

Atom	x	y	z
Co	0.38441(4)	0.1827(1)	0.62564(8)
S(1)	0.4412(1)	0.3706(2)	0.6305(2)
S(2)	0.33775(8)	−0.0245(2)	0.5841(2)
S(3)	0.3835(1)	0.1607(3)	0.7953(2)
N(1)	0.3821(2)	0.2482(7)	0.4893(5)
N(2)	0.4311(2)	0.0305(7)	0.6152(5)
N(3)	0.3309(2)	0.3045(7)	0.6552(5)
C(11)	0.4141(3)	0.3600(8)	0.5035(6)
C(12)	0.4213(3)	0.4440(9)	0.4221(7)
C(13)	0.3961(4)	0.407(1)	0.3281(8)
C(14)	0.3639(3)	0.288(1)	0.3128(7)
C(15)	0.3577(3)	0.2127(9)	0.3969(7)
C(21)	0.4006(3)	−0.0819(9)	0.5948(6)
C(22)	0.4198(4)	−0.2184(9)	0.5865(7)
C(23)	0.4713(4)	−0.233(1)	0.6004(8)
C(24)	0.5028(3)	−0.116(1)	0.6179(7)
C(25)	0.4821(3)	0.016(1)	0.6264(6)
C(31)	0.3342(3)	0.2782(9)	0.7544(7)
C(32)	0.3001(4)	0.345(1)	0.8086(8)
C(33)	0.2661(4)	0.439(1)	0.756(1)
C(34)	0.2642(3)	0.468(1)	0.655(1)
C(35)	0.2973(3)	0.396(1)	0.6047(7)

TABLE 4. Comparison of selected bond lengths (Å) and angles (°) for [Co(2-SC_5H_3N-3-$SiMe_3$)$_3$] and [Co(2-SC_5H_4N)$_3$]

	[Co(2-SC_5H_3N-3-$SiMe_3$)$_3$]	[Co(2-SC_5H_4N)$_3$]
Co–S1	2.241(8)	2.312(3)
Co–S2	2.288(8)	2.313(3)
Co–S3	2.315(8)	2.292(3)
Co–N1	1.91(1)	1.921(6)
Co–N2	1.90(1)	1.912(6)
Co–N3	1.86(1)	1.923(6)
S1–C11	1.77(2)	1.728(9)
S2–C21	1.73(2)	1.741(8)
S3–C31	1.73(2)	1.724(9)
Si–C	1.83(4)	
S1–Co–S2	97.3(3)	99.6(1)
S1–Co–S3	95.8(3)	93.5(1)
S1–Co–N1	72.6(7)	72.7(2)
S1–Co–N2	164.6(3)	166.3(2)
S1–Co–N3	94.7(7)	97.7(2)
S2–Co–S3	164.9(7)	164.36(9)
S2–Co–N1	91.8(7)	96.7(2)
S2–Co–N2	70.8(7)	71.9(2)
S2–Co–N3	99.5(8)	97.7(2)
S3–Co–N1	97.7(7)	99.1(2)
S3–Co–N2	97.4(7)	93.0(2)
S3–Co–N3	71.4(8)	71.9(2)
N1–Co–N2	98.0(9)	96.6(3)
N1–Co–N3	164.0(9)	166.8(3)
N2–Co–N3	96.3(9)	94.2(2)

the trimethylsilyl unit must be introduced at the 3-position to effect gross structural changes. However, the Co–S bond distances associated with [Co(2-SC_5H_3N-3-$SiMe_3$)$_3$] are marginally *shorter* than those of [Co(2-SC_5H_4N)$_3$], 2.28(1) Å compared to 2.305(5) Å, an observation which supports the conclusion that the Co(III) oxidation state is more stable in the case of the bulkier ligand. Although this result is consistent with the general tendency of sterically hindered thiolates to stabilize higher oxidation states, the origin of this effect remains problematical and in this specific instance may reflect an electronic effect, the β-silicon effect of the substituent, in addition to the steric influence.

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