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[$Hg_5(\mu_2\text{-}Cy_2P)_5(O_3SCF_3)_5$] AND [$Hg_5(\mu_2\text{-}Cy_2P)_5(SO_4H)_5$]: COMPOUNDS INVOLVING THE NEW TEN-MEMBERED RING SYSTEM $(Hg\text{–}P)_5$

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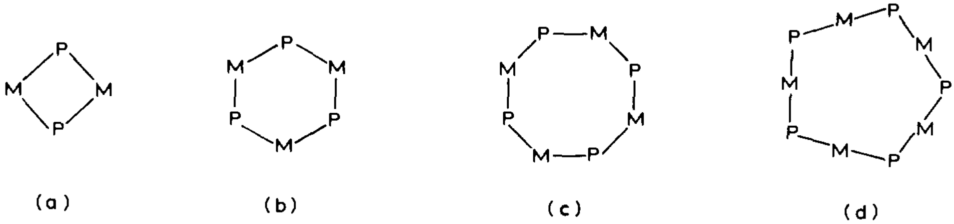
Summary

The reaction of HgX_2 ($X = O_3SCF_3$, $\frac{1}{2}SO_4$, OAc) and dicyclohexylphosphine leads to phosphido-bridged ring pentamers [$Hg_5(\mu_2\text{-}Cy_2P)_5X_5$], $X = O_3SCF_3$, SO_4H or tetramers [$Hg_4(\mu_2\text{-}Cy_2P)_4(OAc)_4$] involving the ten-membered $(Hg\text{–}P)_5$ or eight-membered $(Hg\text{–}P)_4$ heterocycles. The ring size of these "macrocycles" is under thermodynamic control: The P–Hg–P bonding angles seem to depend on the ligating power of X. The ring structures were characterized by ^{31}P and ^{199}Hg NMR spectroscopy.

Introduction

Most of the phosphido bridged ring oligomers $[M(\mu_2\text{-}PR_2)L_m]_n$ adopt a four-membered structure $(M\text{–}P)_2$ (a) [1–3]. In contrast few examples of six-membered ring trimers $(M\text{–}P)_3$ (b) are known [4–8]. We reported recently on the first eight-membered ring structures $(M\text{–}P)_4$ (c) present in the compounds [$Hg_4(\mu_2\text{-}PR_2)L_4$] (R = Cy or Ph, LH = 1,3-bis(2-fluorophenyl)triazene) [8]. This paper describes the first ten-membered ring pentamers $(M\text{–}P)_5$ (d).



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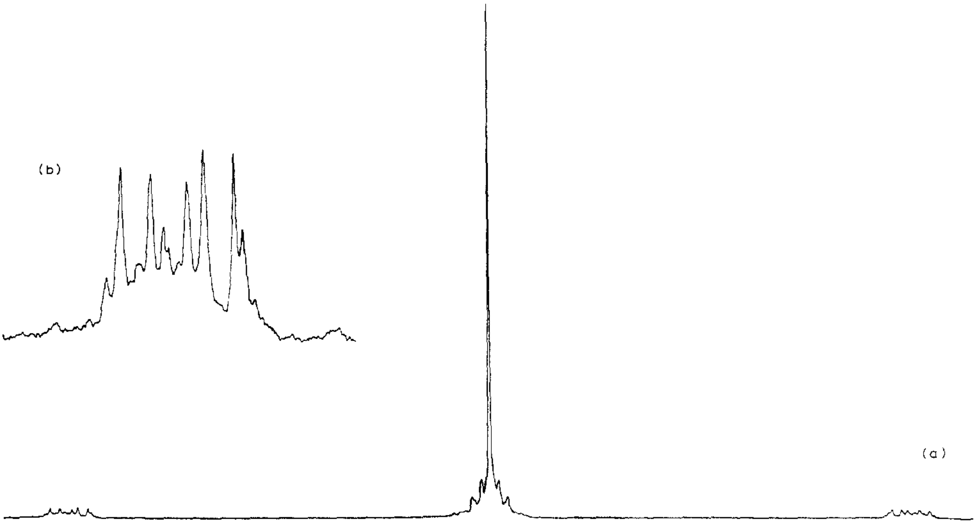


Fig. 1. (a) Experimental $^{31}P\{^1H\}$ NMR spectrum of $[Hg_5(\mu_2\text{-}Cy_2P)_5(SO_4H)_5]$; (b) ^{199}Hg satellite pattern enlarged.

Results and discussion

Mercury(II) sulfate reacts quantitatively with dicyclohexylphosphine in methanol according to eq. 1. Although the acidity of secondary phosphines has been reported

$$HgSO_4 + Cy_2PH \rightarrow Cy_2PHgSO_4H \qquad (1)$$

[9] to increase upon coordination to a metal centre, reaction 1 is clearly favoured by the strength of the mercury-phosphorus bond. The product readily dissolves in methanol. The $^{31}P\{^1H\}$ and $^{199}Hg\{^1H\}$ NMR spectra are shown in Fig. 1 and 2. The complicated ^{199}Hg satellite pattern with an increased intensity, in the ^{31}P NMR spectrum, as well as the ^{199}Hg NMR spectrum consisting of a triplet with a fine structure, indicate an oligomeric $(Hg\text{-}P)_n$ structure. The ^{31}P and ^{199}Hg NMR spectra

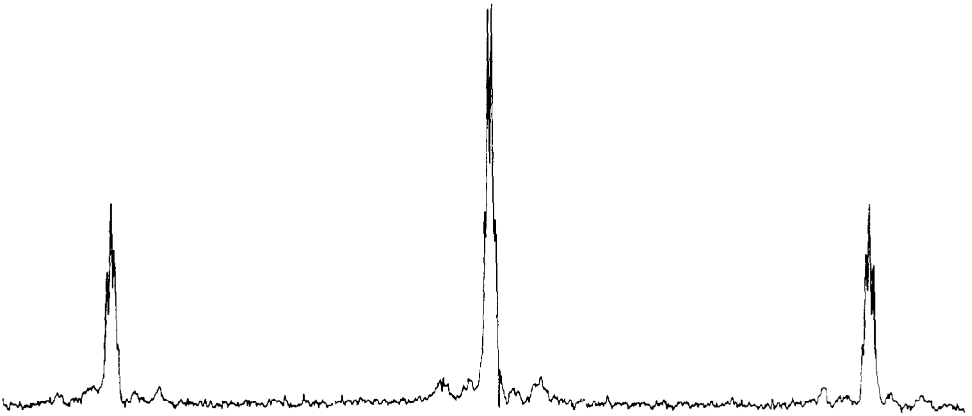


Fig. 2. Experimental $^{199}Hg\{^1H\}$ NMR spectrum of $[Hg_5(\mu_2\text{-}Cy_2P)_5(SO_4H)_5]$.

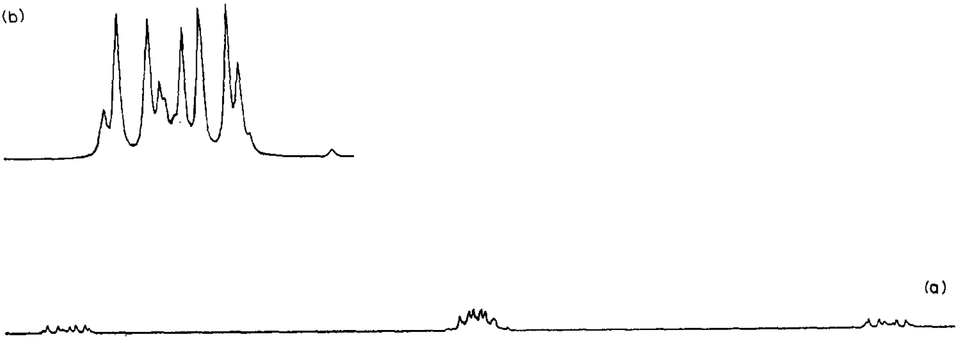


Fig. 3. (a) Calculated ^{31}P NMR spectrum for the (Hg–P)$_5$ ring system of [^{199}Hg$_1$][Hg$_5$(μ_2-Cy$_2$P)$_5$(SO$_4$H)$_5$]; (b) ^{199}Hg satellite pattern enlarged.

were found to be consistent with that calculated for the pentamer involving a (Hg–P)$_5$ ring system: $\delta(^{31}P)$ 64.3, $\delta(^{199}Hg)$ 1494, $^{1}J(^{199}Hg, ^{31}P)$ 3165, $^{2}J(^{31}P, ^{31}P)$ 137, $^{3}J(^{199}Hg, ^{31}P)$ 44, $^{4}J(^{31}P, ^{31}P)$ 3, $^{5}J(^{199}Hg, ^{31}P)$ 19; 0.1 mmol/cm^{-3} MeOH.

Figures 3 and 4 show the ^{31}P and ^{199}Hg NMR spectra calculated for the isotopomer with one ^{199}Hg atom ($p_1 = 40.3\%$, natural abundance of ^{199}Hg: 16.8%). The other isotopomers containing ^{199}Hg atoms with a total propability of 20% are not resolved in the experimental ^{31}P NMR spectrum. No exchange processes involving the Hg–P bonds occur on the NMR time scale at ambient temperature. The (M–P)$_5$ heterocyclus was previously unknown for mercury and other metals.

The reaction of mercury(II) trifluoromethanesulfonate (as DMSO complex) and dicyclohexylphosphine in methanol similarly gives a quantitative yield of a colorless crystalline precipitate which analyzes for Cy$_2$PHgO$_3$SCF$_3$ (eq. 2).

$$Hg(O_3SCF_3)_2 + Cy_2PH \xrightarrow{MeOH} Cy_2PHgO_3SCF_3 + HO_3SCF_3 \qquad (2)$$

A second equivalent of Cy$_2$PH does not give the corresponding symmetric compound Hg(PCy$_2$)$_2$ or coordination complexes [Cy$_2$PHg(Cy$_2$PH)$_n$](O$_3$SCF$_3$). The

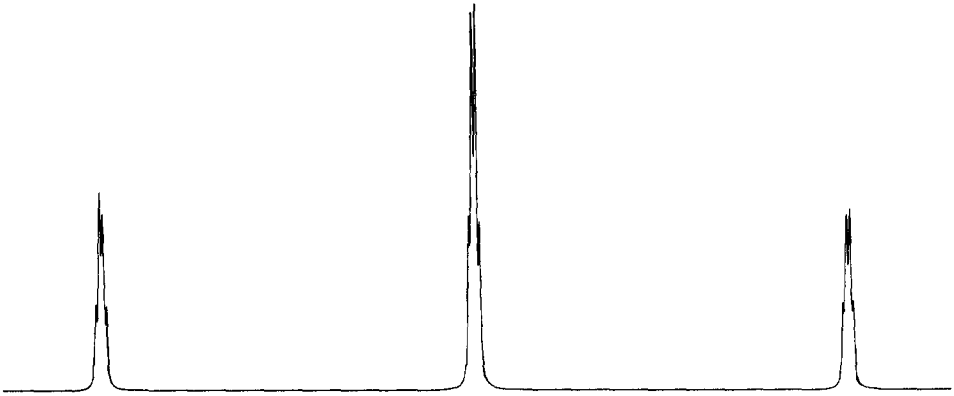


Fig. 4. Calculated ^{199}Hg NMR spectrum for the (Hg–P)$_5$ ring system of [^{199}Hg$_1$][Hg$_5$(μ_2-Cy$_2$P)$_5$-(SO$_4$H)$_5$].

reaction of mercury(II) trifluoromethanesulfonate and dicyclohexylphosphine in dichloromethane yields a clear solution. NMR spectroscopy reveals the existence of equilibrium 3. This equilibrium is far to the right, the components on the left hand

$$\mathrm{Hg(O_3SCF_3)_2 + Cy_2PH \xrightleftharpoons{CH_2Cl_2} Cy_2PHgO_3SCF_3 + HO_3SCF_3} \qquad (3)$$

side forming a coordination complex. Reaction 3 is shifted completely to the right upon addition of a base, such as HgO (eq. 4).

$$\mathrm{Hg(O_3SCF_3)_2 + HgO + 2\,Cy_2PH \rightarrow 2Cy_2PHgO_3SCF_3 + H_2O} \qquad (4)$$

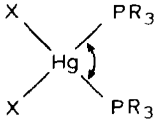
The ^{31}P and ^{199}Hg NMR spectra of $Cy_2PHgO_3SCF_3$ again exhibit the pattern of the $(Hg-P)_5$ ring system: $\delta(^{31}P)$ 70.4, $\delta(^{199}Hg)$ 1531, $^1J(^{199}Hg, ^{31}P)$ 3004, $^2J(^{31}P, ^{31}P)$ 136, $^3J(^{199}Hg, ^{31}P)$ 61, $^4J(^{31}P, ^{31}P)$ 2, $^5J(^{199}Hg, ^{31}P)$ 27; 0.05 mmol/cm^{-3} CH_2Cl_2.

On the other hand $Cy_2PHgOAc$ formed by reaction 5 in different solvents (e.g.

$$\mathrm{Hg(OAc)_2 + Cy_2PH \rightarrow Cy_2PHgOAc + HOAc} \qquad (5)$$

methanol or dichloromethane) has a tetrameric structure involving the eight-membered $(Hg-P)_4$ ring, as shown by its $^{31}P\{^1H\}$ and $^{199}Hg\{^1H\}$ NMR patterns in Figs. 5 and 6: $\delta(^{31}P)$ 55.4, $\delta(^{199}Hg)$ 1634, $^1J(^{199}Hg, ^{31}P)$ 3237, $^2J(^{31}P, ^{31}P)$ 133, $^3J(^{199}Hg, ^{31}P)$ 44, $^4J(^{31}P, ^{31}P)$ ~ 0; 0.125 mmol/cm^{-3} MeOH. The ^{31}P NMR spectrum displays a ^{199}Hg satellite pattern characteristic of a $(Hg-P)_4$ system [8]. The ^{199}Hg NMR spectrum consists of almost first order triplets of triplets due to the isotopomer with one ^{199}Hg atom coupling with 2 phosphorus atoms through one bond and with two phosphorus atoms through 3 bonds. Figures 7 and 8 show the ^{31}P and ^{199}Hg NMR spectra calculated for the isotopomer with one ^{199}Hg atom.

The ring sizes can be rationalized as follows: The P–Hg–P bonding angle in the



(e)

addition complexes $[HgX_2(PR_3)_2]$ (e) has been found to increase with decreasing ligating power of X [10,11]. A series of X-ray structure determinations on

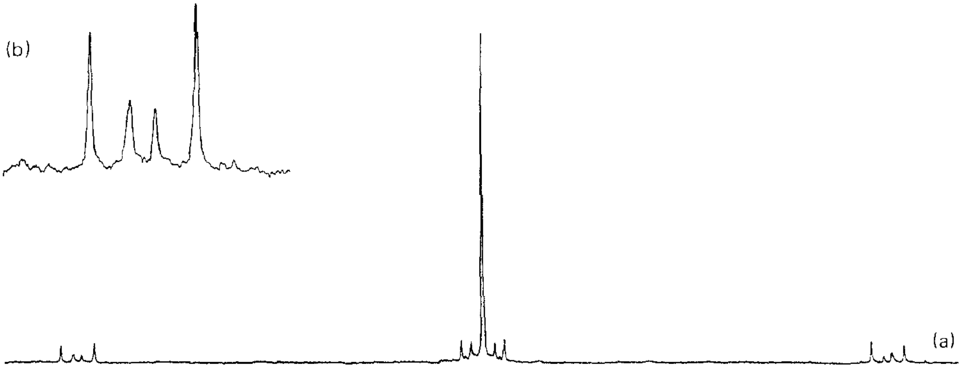


Fig. 5. (a) Experimental $^{31}P\{^1H\}$ NMR spectrum of $[Hg_4(\mu_2\text{-}Cy_2P)_4(OAc)_4]$; (b) ^{199}Hg satellite pattern enlarged.

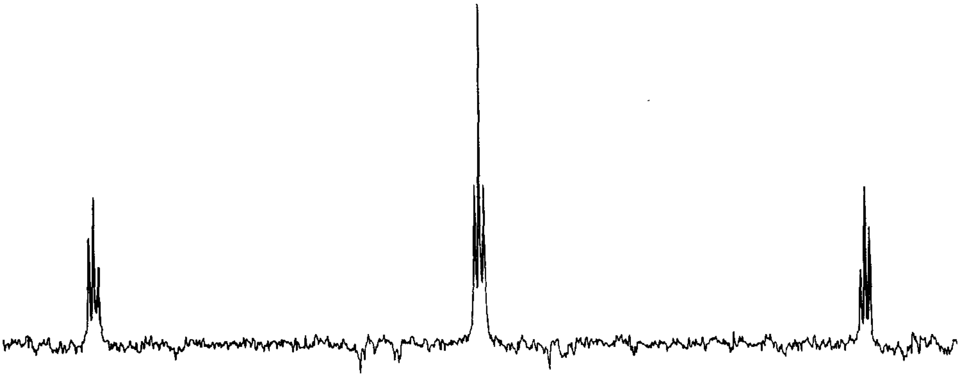


Fig. 6. Experimental $^{199}Hg\{^1H\}$ NMR spectrum of $[Hg_4(\mu_2\text{-}Cy_2P)_4(OAc)_4]$.

$[HgX_2(PPh_3)_2]$ systems showed that the P–Hg–P angle decreases in the order X = NO_3 (132°) > SCN (118°) > I (109°) ~ CN (109°) > CF_3 (95°), i.e. in the order of increasing bond strength of X [10,12,13]. A linear P–Hg–P configuration is assumed for cations $[Hg(PR_3)_2]^{2+}$ with uncoordinated counterions [11]. $[Hg(PCy_3)_2](ClO_4)_2$ contains 2-coordinate mercury atoms (P–Hg–P 171°) and Hg–O distances lying outside the sum of the Van der Waals radii (290 pm). In $Hg(PCy_3)_2(OAc)_2H_2O$ the P–Hg–P bonding angle is considerably distorted from linearity (153 and 146°) and the acetate group is bound to mercury (Hg–O: 245 and 241 pm) [14].

A similar correlation should apply to the ring oligomers $(PR_2HgX)_n$ (f). The P–Hg–P bonding angles depending on X would thus result in different $(Hg–P)_n$ ring sizes.

Trifluoromethanesulfonate and hydrogensulfate are both considered to be non-coordinating anions in PCy_2HgX for the following reasons: $[Hg(DMSO)_6](O_3SCF_3)_2$ and $HgSO_4$ coordinate up to 4 molecules of tributylphosphine [15]. This is the maximum coordination number and is reached only for non-coordinating counter-

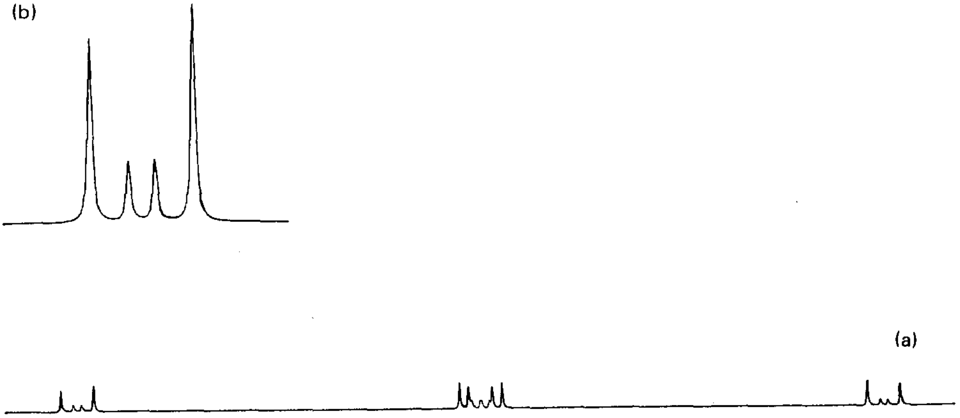


Fig. 7. (a) Calculated ^{31}P NMR spectrum for the $(Hg–P)_4$ ring system of $[^{199}Hg_1][Hg_4(\mu_2\text{-}Cy_2P)_4(OAc)_4]$; (b) ^{199}Hg satellite pattern enlarged.

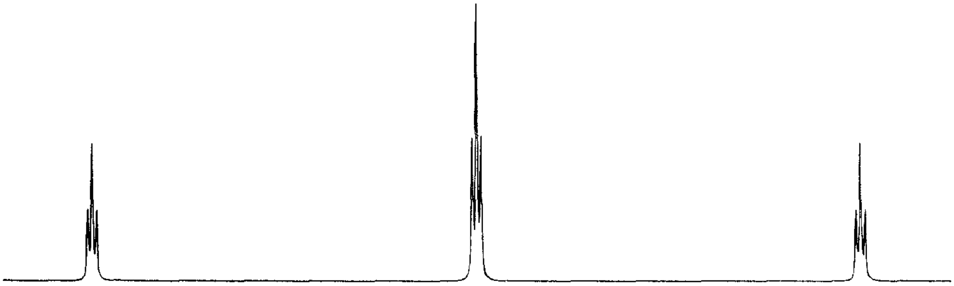
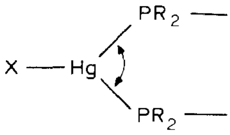


Fig. 8. Calculated ^{199}Hg NMR spectrum for the (Hg–P)$_4$ ring system of [^{199}Hg$_1$][Hg$_4$(μ_2-Cy$_2$P)$_4$(OAc)$_4$].

ions [16]. Mercury(II) acetate coordinates only 3 molecules of PBu$_3$, which indicates the involvement of the acetate group in the coordination of mercury [16]. Secondly the one bond mercury–phosphorus coupling in [HgX$_2$(PR$_3$)$_2$] has been correlated



(f)

with the P–Hg–P bonding angle: the coupling constant increases with increasing P–Hg–P angle in the order CN < I < SCN < OAc < NO$_3$ [10], but decreases for the even more linear species [Hg(PR$_3$)$_2$]$^{2+}$ with non-coordinating anions [17]. The couplings of [Hg(PBu$_3$)$_2$]X$_2$, X = O$_3$SCF$_3$ or $\frac{1}{2}$SO$_4$ are both smaller than for X = OAc indicating thus more linear P–Hg–P elements [15].

A linear P–Hg–P configuration in Cy$_2$PHgX, X = O$_3$SCF$_3$ or SO$_4$H is thus assumed and this would easily be accommodated in the ten-membered ring of type d, which combines a linear P–Hg–P element together with an approximately tetrahedral Hg–P–Hg angle (regular pentahedron: 108°).

Experimental

The NMR spectra were recorded on a multinuclear Bruker WP-80 spectrometer in the FT mode and calculated using PANIC on a Bruker Aspect 2000 computer. Chemical shifts are in ppm to high frequency of 85% H$_3$PO$_4$ or aqueous Hg(ClO$_4$)$_2$ (2 mmol HgO/cm^{-3} 60% HClO$_4$), coupling constants in Hz.

[Hg(DMSO)$_6$](O$_3$SCF$_3$)$_2$ was prepared by a published method [18] and the other reagents were commercial obtained. All operations were carried out under nitrogen in degassed solvents.

Cy$_2$PHgO$_3$SCF$_3$. 50 mg (0.25 mmol) of dicyclohexylphosphine is added to a solution 242 mg (0.25 mmol) of [Hg(DMSO)$_6$](O$_3$SCF$_3$)$_2$ in 2 cm^3 of methanol. The colorless crystalline product starts to precipitate immediately. After stirring the mixture for 30 minutes the product is filtered off and washed with methanol. Yield, almost quantitative, m.p. 285°C (dec.), Analysis. Found: C, 28.7; H, 4.4: C$_{13}$H$_{22}$F$_3$HgO$_3$PS calcd.: C, 28.5; H, 4.1%.

Cy_2PHgSO_4H. Treatment of 74 mg (0.25 mmol) of $HgSO_4$ with 50 mg of dicyclohexylphosphine in 2 cm^3 of methanol yields a clear solution of the product after shaking for 15 minutes. Evaporation of the solvent gives the required product as an oil.

$Cy_2PHgOAc$. 80 mg (0.25 mmol) of $Hg(OAc)_2$ and 50 mg (0.25 mmol) of dicyclohexylphosphine are mixed in 2 cm^3 of dichloromethane. Evaporation of the solvent yields a glassy solid which crystallizes upon addition of a few drops of pyridine. The product is filtered off and dried in vacuo. Yield ca. 90%, m.p. 140°C (dec.). Analysis. Found: C, 36.6; H, 5.5. $C_{14}H_{25}HgO_2P$ calcd.: C, 36.8; H, 5.5%.

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