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Quinoneimido Complexes of a Metalloporphyrin: Isolation, X-ray Crystal Structures, and DFT Calculations

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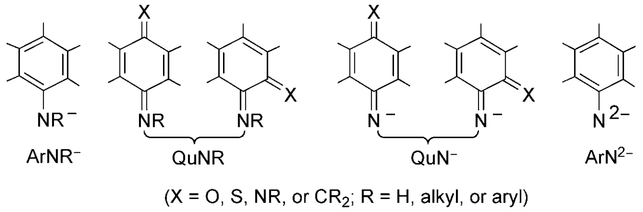
Quinoneimine and quinoneimido ligands (designated here as QuNR and QuN$^-$, respectively) bear close relevance to arylamido (ArNR$^-$) and arylimido (ArN^{2-}) ligands (Scheme 1).[1] The latter two have been subjected to immense studies in the field of metal–ligand multiple-bonded complexes and in metal-catalyzed nitrogen/group-transfer catalysis.[2] While there are a large number of metal complexes of quinoneimines known in the literature,[3,4] quinoneimido complexes of transition metals are sparse.[5–7] In the early 1990s, Sharp and co-workers[5a,b] reported di- or tetranuclear rhodium complexes analogous to bridging quinoneimido complexes. Subsequently, bridging quinoneimido ligands were reported to exist in a few di- or trinuclear osmium[5c] and palladium/platinum[5d] complexes and hexanuclear osmium complexes,[5e] with the oxidation states of the metal ions being +2 or less. Terminal quinoneimido complexes of transition metals are extremely rare, which were once considered (as hypothetical species) in the oxidation of nickel *o*-phenylenediamine complexes[8] and were proposed to be the key intermediates in dirhodium-catalyzed carbazole formation from biaryl azides.[9] To the best of our knowledge, only one transition-metal complex bearing a terminal quinoneimido ligand has been isolated and reported in literature, that is, a mono(quinoneimido) nickel(II) complex recently reported by Stephan and Bai.[6] Herein we report the isolation, spectroscopy, and X-ray crystal structures of several terminal quinoneimido complexes of ruthenium(IV), which constitute the first quinoneimido complexes of a metalloporphyrin.



Scheme 1. Quinoneimine, quinoneimido, arylamido, and arylimido ligands.

Our approach to quinoneimido complexes came from an unexpected reaction of high-valent metal-oxo complexes [Ru^{VI}(por)O$_2$] (por = porphyrinato^{2-}) with an aniline derivative, in contrast to the formation of the mono(quinoneimido) nickel(II) complex from reaction of a β-diketiminate nickel(II) complex with an aryl azide.[6] We previously reported that [Ru^{VI}(por)O$_2$] reacts with *para*-substituted anilines to afford bis(arylamido)ruthenium(IV) porphyrins [Ru^{IV}(por)(NH-*p*-RC$_6$H$_4$)$_2$] (R = Cl, NO$_2$; Scheme 2),[10a] a reactivity similar to the formation of [Ru^{IV}(por)(NPh$_2$)$_2$] from the reaction between [Ru^{VI}(por)O$_2$] and Ph$_2$NH.[10b] However, attempts to extend such reactivity of [Ru^{VI}(por)O$_2$] to 2,6-dimethylaniline did not lead to the formation of arylamido complexes [Ru^{IV}(por)(NH-2,6-Me$_2$C$_6$H$_3$)$_2$]. Strikingly, the products obtained were ruthenium porphyrins bearing terminal quinoneimido groups.

Treatment of [Ru^{VI}(por)O$_2$] (por = ttp,[11a] 4-MeO-tpp,[11b] 4-Cl-tpp[11c]) with 20 equiv of 2,6-dimethylaniline in ethanol for 8 h produced a red purple precipitate, which was found to be a mixture of quinoneimido complexes [Ru^{IV}(por)(NQu)(OEt)] (por = ttp: **1a**; 4-MeO-tpp: **1b**; 4-Cl-tpp: **1c**) and [Ru^{IV}(por)(NQu)(OH)] (por = ttp: **2a**; 4-MeO-tpp: **2b**; 4-Cl-tpp: **2c**) (yield ≈ 65 %). Complexes **2** probably resulted from the hydrolysis of **1** owing to the presence of a trace amount of water in the solvent. Indeed, stirring a mixture of

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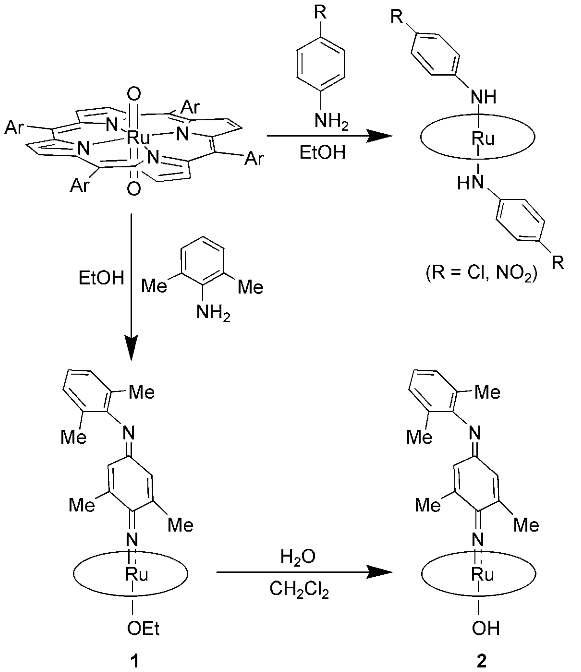


Scheme 2. Formation of quinoneimido ruthenium(IV) complexes.

1 and **2** in dichloromethane/water (10:1 v/v) for 0.5 h completely converted **1** into **2**.

Both **1** and **2** exhibit well-resolved diamagnetic ^1H NMR spectra (Figure 1, and Figure S1 in the Supporting Information), featuring substantially upfield-shifted H^d and $H^{d'}$ signals ($\delta \approx 4.3$, 3.5 ppm) compared with the corresponding signals of arylamido complex $[Ru^{IV}(ttp)(NH\text{-}p\text{-}ClC_6H_4)_2]$ ($\delta =$ 5.84 ppm[10a]), which is consistent with the attachment of H^d and $H^{d'}$ to a quinone-like ring.[5a,b] The large splitting of the H^d and $H^{d'}$ signals should stem from the prohibited rotation of the 2,6-dimethylphenyl group about the directly attached C═N bond (which also splits the Me^2 and $Me^{2'}$ signals as observed). Owing to the unsymmetrical coordination of the axial sites, the H^b and $H^{b'}$ atoms of the *meso*-tolyl groups give different signals. The H^a signal ($\delta = 8.71$ ppm) of **2a** appears at a lower field than those of $[Ru^{IV}(ttp)(NH\text{-}p\text{-}ClC_6H_4)_2]$ ($\delta = 8.41$ ppm[10a]) and methyleneamido complex $[Ru^{IV}(ttp)(N{=}CPh_2)(OH)]$ ($\delta = 8.61$ ppm[12]).

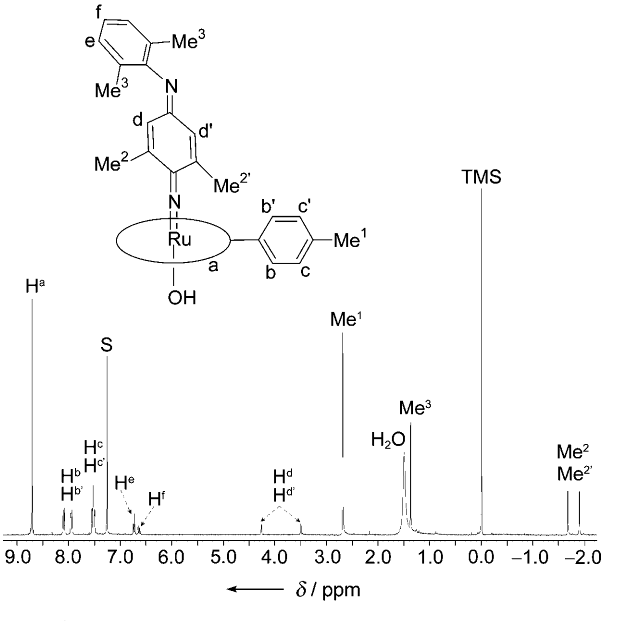


Figure 1. ^1H NMR spectrum of **2a** in $CDCl_3$.

UV/Vis spectra of **2a–c** feature Soret and β bands at λ_{max} ≈ 420 and 530 nm, respectively (Figure S2 in the Supporting Informaion), similar to those of $[Ru^{IV}(ttp)(NH\text{-}p\text{-}ClC_6H_4)_2]$ (416 and 529 nm)[10a] and $[Ru^{IV}(ttp)(N{=}CPh_2)(OH)]$ (419 and 527 nm).[12] The IR spectra of **2a–c** exhibit oxidation state marker bands[10a] at 1012–1015 cm^{-1}, consistent with a Ru^{IV} formulation.[10a,12] In the electrospray mass spectra of **2a–c**, intense cluster peaks attributable to $[Ru(por)(NQu)]^+$ were observed (Figures S3 and S4 in the Supporting Information).

The X-ray crystal structures of **1a**·2EtOH and **1b**·1.5H_2O were determined (Figure 2; see also Table S1 and Figures S5 and S6 in the Supporting Information).[13] Despite the disorder of the peripheral 2,6-dimethylphenyl group of the quinoneimido ligand in **1a**·2EtOH and the ethyl group of EtO^- in **1b**·1.5H_2O, a combination of the structural information obtained from the two crystals could well provide structural features of a $[Ru^{IV}(por)(NQu)(OEt)]$ species.

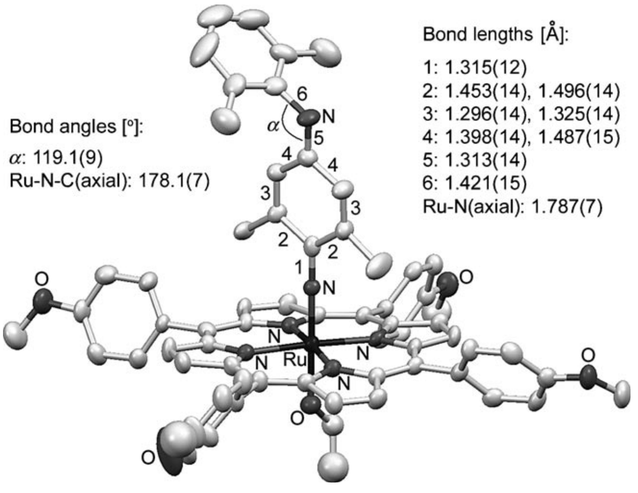


Figure 2. Structure of **1b**·1.5H_2O with omission of hydrogen atoms and solvent molecules. Ellipsoids are represented at the 30 % probability level.

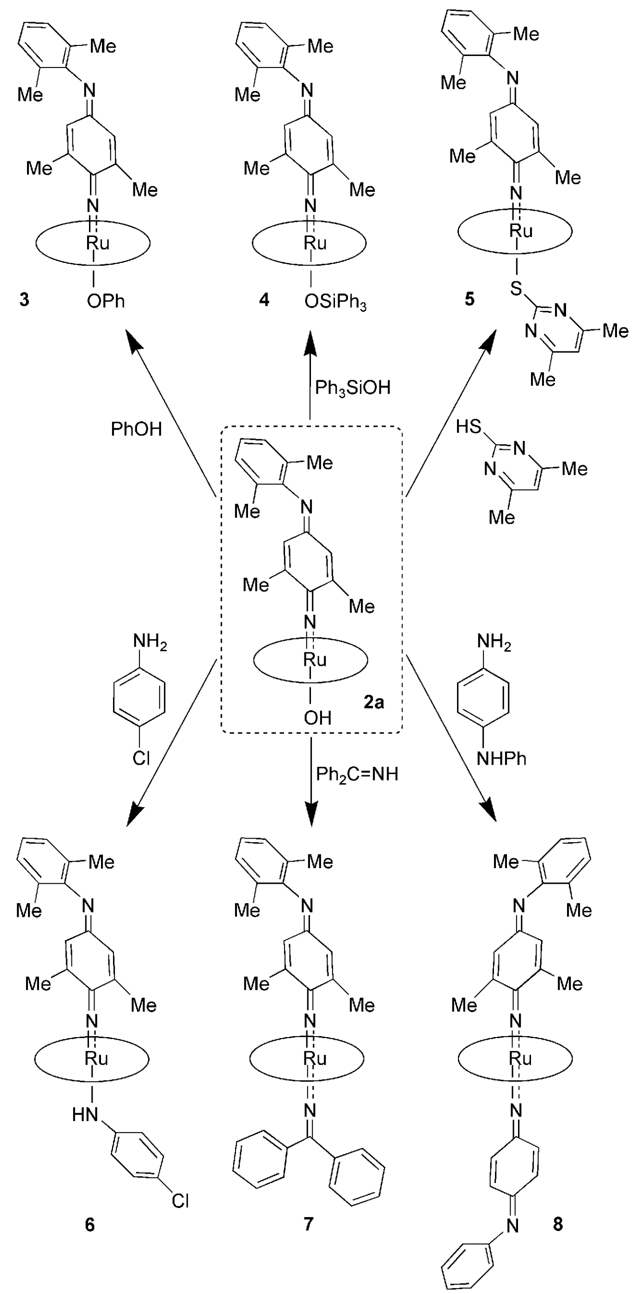
Like the mono(quinoneimido) nickel(II) complex,[6] **1a**,**b** each contain a linear terminal quinoneimido group (Ru-*N*-C: 179.8(4)° for **1a** and 178.1(7)° for **1b**), with a short Ru–N(quinoneimido) distance of 1.80(2) Å for **1a** and 1.787(7) Å for **1b**. These geometric parameters are comparable to those of the linear arylimido complex $[(\eta^6\text{-cymene})Ru{=}N\text{-}2,4,6\text{-}tBu_3C_6H_2]$ (Ru-*N*-C: 177.8(4)°; Ru-N(arylimido): 1.753(3) Å)[14] and linear methyleneamido complex

$[Ru^{IV}(tpp)(N{=}CPh_2)(OH)]$ (Ru-*N*-C: 175.0(4)°; Ru-N(methyleneamido): 1.808(4) Å).[12] The bond lengths and α angle shown in Figure 2 agree well with the quinoneimido core. The Ru−OEt distances of 1.92(3) (**1a**) and 1.914(7) Å (**1b**) fall within the range of 1.892(3)–1.947(11) Å observed for the Ru−OR distances in $[\{Ru^{IV}(por)(O\text{-}p\text{-}MeC_6H_4)\}_2O]$[15a] and $[Ru^{IV}(por)(OiPr)_2]$.[15b]

Complexes **2** are air-stable both in the solid state and in solution. Their quinoneimido groups are remarkably inert toward attack by protons. For example, treatment of **1a** or **2a** with CF_3COOH at room temperature for several hours did not cleave the Ru−N(quinoneimido) bond, as revealed by ^1H NMR spectroscopic analysis. These demonstrate the remarkable ability of a terminal quinoneimido ligand to stabilize a high-valent metal ion. ^1H NMR measurements (Figures S7–S11 in the Supporting Information) also reveal that the axial HO^- group in **2a** is reactive toward a variety of protic reagents including PhOH, Ph_3SiOH, (dmpym)SH (4,6-dimethylpyrimidine-2-thiol), $p\text{-}ClC_6H_4NH_2$, and $Ph_2C{=}NH$ to afford $[Ru^{IV}(ttp)(NQu)(X)]$ ($X^-=PhO^-$: **3**; Ph_3SiO^-: **4**; $(dmpym)S^-$: **5**; $p\text{-}ClC_6H_4NH^-$: **6**; and $Ph_2C{=}N^-$: **7**; Scheme 3),[16] thus providing a unique access to ruthenium(IV) porphyrins that contain an alkoxide, arylamido group, thiolate, or methyleneamido group *trans* to a quinoneimido group.

Interestingly, reaction of **2a** with *N*-phenyl-benzene-1,4-diamine ($C_6H_5NH\text{-}p\text{-}C_6H_4NH_2$) in dichloromethane for two days resulted in the formation of bis(quinoneimido) complex $[Ru^{IV}(ttp)(NQu)(NQu')]$ (**8**, Scheme 3). Work-up gave **8** as a purple solid contaminated by ca. 10 mol % of **2a**, as revealed by its ^1H NMR spectrum (Figure S12 in the Supporting Information).[17] The mass spectrum of **8** shows prominent cluster peaks at *m*/*z* 1188 $[M]^+$ and 1007 $[M{-}NQu']^+$. To the best of our knowledge, complex **8** is the first example of directly observed bis(quinoneimido) complexes of a transition metal.

To examine the extent of electron delocalization over the $QuN\text{-}Ru^{IV}\text{-}OEt$ or $QuN\text{-}Ru^{IV}\text{-}NQu'$ moiety in **1** and **8**, we performed density functional theory (DFT) calculations on model compounds **9** and **10** (Figure 3). As the $QuN\text{-}Ru^{IV}\text{-}NQu'$ moiety in **8** could be viewed as a model for metal-doped oligoanilines, we also carried out DFT calculations on model compound **11** (Figure 3). The optimized structure of **9** (see Table S3 in the Supporting Information) agrees well with the X-ray crystallographic data of **1a**,**b** (within 0.026 Å root-mean-square deviations over all heavy atoms). Replacing the MeO^- axial ligand in **9** with $Qu'N^-$ to form **10** lengthens the Ru−N(quinoneimido) bond by ca. 0.057 Å, accompanied by a slight increase and decrease of C−N and C=N bond lengths, respectively (see Table S3 in the Supporting Information). From the MO surfaces of the HOMOs shown in Figure 4 (see also Tables S4 and S5 in the Supporting Information), it can be seen that both **9** and **10** have the electron density delocalized over the whole Qu'N-Ru-OMe or $Qu'N\text{-}Ru^{IV}\text{-}NQu'$ chain, and the delocalization becomes more prominent in the case of **10**. The π-bonding orbitals between Ru and N (and also O in the case of **9**) are occupied, with the antibonding counterparts being the LUMOs (Figure 4). A comparison of the computed bond lengths (Table S6 in the Supporting Information) and bond angles (Figure 3) between **11** and the Qu'N-Ru-NQu' moiety in **10** reveals that the "Ru doping" (i.e. replacing the middle phenyl group of **11** by a Ru^{IV} ion) considerably shortens the nearest C=N bonds by 0.025 Å (other bond lengths are little changed) and markedly straightens the molecular chain. This can be attributed to the π-bonding interaction between the redox-active Ru^{IV} center and the N atom of the quinoneimido groups.



Scheme 3. Reactions of **2a** with various protic reagents.

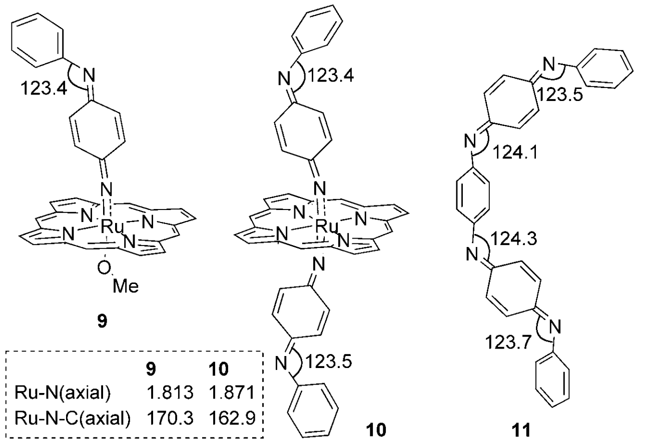


Figure 3. Optimized structures of **9**–**11** by DFT calculations. The key bond lengths [Å] and angles [°] are indicated.

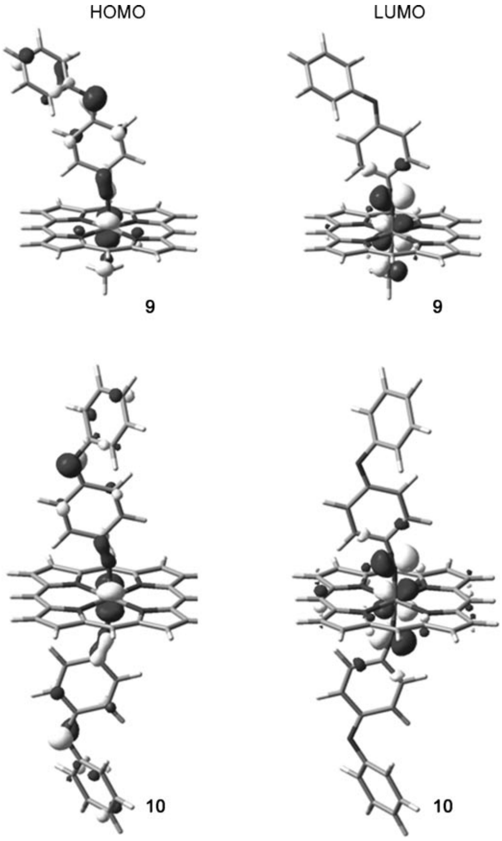


Figure 4. HOMO and LUMO surfaces of **9** and **10**.

In summary, we have isolated and structurally characterized quinoneimido complexes of a metalloporphyrin. The generation of a quinoneimido ligand from the reaction of $[Ru^{VI}(por)O_2]$ with an arylamine[18] is a C=N bond-formation process mediated by ruthenium porphyrins, and provides useful insight into the oxidation chemistry of aryl amines by oxometalloporphyrins. These reactions could be related to the formation of quinoneimines from electrochemical[19]/metal-promoted[3c,20] oxidative dimerization of anilines or from nucleophilic attack of coordinated amido groups by amines.[1c] Particularly intriguing are the *trans* bis(quinoneimido) ruthenium complexes, as the redox behavior of the bis(quinoneimido) chains could provide useful information about the effect of doping a redox-active metal ion into oligoanilines.

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Keywords: density functional calculations • N ligands • porphyrins • quinoneimido complexes • ruthenium

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[16] Coordination of the X^- groups to [Ru(ttp)] (in **3**–**7**) is indicated by the large upfield shifts of their proton resonances, relative to the corresponding free XH, as a result of the porphyrin ring current effect. The diamagnetic ^{1}H NMR spectra of **3**–**7** preclude formulation of these complexes as [Ru^{III}(ttp)(NQu)(XH)]. Importantly, the ^{1}H NMR spectrum of **7** shows a single set of signals for the [Ph_2C=N] moiety (Figure S11 in the Supporting Information), which is incompatible with the coordination of Ph_2C=NH but consistent with the coordination of Ph_2C=N^- (see reference [12]). A comparison of the proton resonances among [Ru^{IV}(ttp)(NQu)(X)] (**1**–**7**, see Table S2 in the Supporting Information) reveals the following effect of X^- groups on the proton resonances of [Ru^{IV}(ttp)(NQu)]: i) The H^a signal for $X^- = HO^-$ is downfield from those for the other X^- groups. ii) The splitting between the H^b and H$^{b'}$ signals is the largest for X = Ph_3SiO^-/(dmpym)S^-/Ph_2C=N^- and the smallest for X = *p*-$ClC_6H_4NH^-$. iii) The H^d, H$^{d'}$, Me^2, Me$^{2'}$ signals of Ru-NQu shift downfield along $X^- = Ph_3SiO^- \rightarrow HO^-$, EtO^-, PhO^-, (dmpym)$S^- \rightarrow$ *p*-$ClC_6H_4NH^- \rightarrow Ph_2C$=$N^-$.

[17] The Ru-NQu proton resonances of **8** are similar to those of **7** (see Table S2 in the Supporting Information). Owing to the presence of an equatorial pseudo-mirror plane in the molecule of **8**, its H^b and H$^{b'}$ signals almost coalesce. The large splitting between the H^g and H$^{g'}$ signals, and between the H^h and H$^{h'}$ signals, precludes alternative formulation of the Qu'N^- group as the arylamido groups C_6H_5NH-*p*-$C_6H_4NH^-$ or [C_6H_5N-*p*-$C_6H_4NH_2$]$^-$.

[18] Preliminary studies showed that [Ru^{VI}(por)O_2] could also react with excess 2,6-dichloroaniline to afford the corresponding quinoneimido complexes. However, no such complexes were obtained by reacting [Ru^{VI}(por)O_2] with excess 2,4,6-trimethylaniline.

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