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# Electrochemistry of Macrocyclic Cobalt(III/II) Hexaamines: Electrocatalytic Hydrogen Evolution in Aqueous Solution

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The macrocyclic cobalt hexaamines [Co(*trans*-diammac)]$^{3+}$ and [Co(*cis*-diammac)]$^{3+}$ (diammac = 6,13-dimethyl-1,4,8,11-tetraazacyclotetradecane-6,13-diamine) are capable of reducing the overpotential for hydrogen evolution on a mercury cathode in aqueous solution. Protons are reduced in a catalytic process involving reoxidation of the Co$^{II}$ species to its parent Co$^{III}$ complex. The cycle is robust at neutral pH with no decomposition of catalyst. The stability of the [Co(*trans*-diammac)]$^{2+}$ and [Co(*cis*-diammac)]$^{2+}$ complexes depends on the pH of the solution and the coordinating properties of the supporting electrolyte. Electrochemical studies indicate that the adsorbed Co$^{II}$ complex on the surface of mercury is the active catalyst for the reduction of protons to dihydrogen.

## Introduction

The use of coordination compounds as electrocatalysts has received considerable attention in recent times.[1,2] The most prolific research has been in the areas of dioxygen reduction to $H_2O_2$ and $H_2O$ through the use of porphyrins,[3,4] and carbon dioxide activation and reduction to a variety of products using macrocyclic complexes,[5−11] acyclic tridentate ligands,[12−16] and porphyrins.[17,18]

The use of coordination compounds as catalysts to evolve dihydrogen from aqueous solution has been achieved by various methods. Some of the earliest polarographic studies involved the observation of hydrogen evolution catalyzed by proteins in the presence of dissolved cobalt salts.[19,20] A number of coordination compounds generate dihydrogen from aqueous solution after being reduced either at a cathode or by an appropriate reducing agent. For example, hydridocobaloximes react with acid to produce dihydrogen,[21] as do various hydridometalloporhyrin complexes.[22−24] Cobalt porphyrins have been attached to electrodes in a variety of ways to measure their electrocatalytic activity,[25,26] and iron porphyrins, when electrochemically reduced to zero oxidation states, are efficient homogeneous catalysts of dihydrogen evolution.[27] The complex $[Os(NH_3)_5(OH_2)]^{2+}$ is short-lived in aqueous solution, being oxidized by acid to produce $H_2$, and adsorption to mercury enhances the rate of proton reduction.[28−30] Nickel and cobalt complexes of macrocyclic ligands are also capable of electrocatalytically producing hydrogen from a mercury cathode in aqueous solution.[31,32] Cobalt hexaamines such as [Co(sep)]$^{3+}$ (sep = 1,3,6,8,10,13,16,19-octaazabicyclo[6.6.6]eicosane) have been reported as electron relays for $H_2$ production from water.[33,34] The advantages of using cobalt hexaamines as electron-transfer agents are their facile electron-transfer kinetics and stability in the II and III oxidation states.

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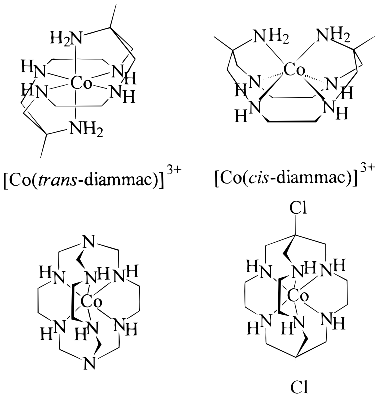
## Chart 1



[Co(*trans*-diammac)]$^{3+}$ [Co(*cis*-diammac)]$^{3+}$

[Co(sep)]$^{3+}$ [Co(diCLsar)]$^{3+}$

We have recently reported the homogeneous redox properties of a series of pendent armed macrocyclic Co$^{III/II}$ hexaamines.[35] The trans isomers of these complexes were found to have self-exchange electron-transfer rates significantly higher than the macrobicyclic cage compounds, whose electrochemistry and redox properties have been studied in detail.[36] We report here the electrochemistry of the macrocyclic complexes [Co(*trans*-diammac)]$^{3+}$ and [Co(*cis*-diammac)]$^{3+}$ in aqueous solution. In particular we demonstrate their stability in the Co$^{II}$ oxidation state, and ability to electrocatalytically evolve dihydrogen from the surface of a mercury cathode.

## Experimental Section

**Materials.** The complexes [Co(*trans*-diammac)](ClO$_4$)$_3$·H$_2$O,[37] [Co(*cis*-diammac)](ClO$_4$)$_3$,[38] [Co(sep)]Cl$_3$,[39] and [Co(diClsar)]Cl$_3$[40] (Chart 1) were synthesized via published procedures. Mercury was triple distilled (Banksia Scientific). Dinitrogen used was of ultrahigh purity. Phosphate buffer used was 0.1 M NaH$_2$PO$_4$/Na$_2$HPO$_4$.

**Physical Methods.** Electrochemistry was performed using a BAS 100 B/W potentiostat controlled by a PC running BAS 100W 2.0 software. Electrodes used for cyclic voltammetry were glassy carbon (Bioanalytical Systems) of area 0.072 cm$^2$ or a hanging mercury drop (Princeton Applied Research 303 SMDE) of mass 1.64 mg with a Ag/AgCl reference electrode and a platinum wire counter electrode. iR compensation was employed for all cyclic voltammetry measurements.[41] Bulk electrolysis was carried out in an 85 mL cell on either reticulated vitreous carbon (Bioanalytical systems) or a mercury pool in contact with a platinum wire as the working electrode, a Ag/AgCl reference electrode, and a platinum coil counter electrode. This counter electrode was separated from the test solution by a glass frit. For the bulk electrolysis experiments on mercury, nitrogen was scrubbed with a metavanadate/Zn(Hg) mixture. Nitrogen was continuously bubbled through the solution during electrolysis, except when hydrogen production was being measured. In this case a homemade vessel of 40 mL capacity was used that was airtight and connected to a manometer. All potentials are reported versus Ag/AgCl unless otherwise stated. Cyclic voltammetry simulations were performed with Digisim 2.0 (Bioanalytical Systems).[42] Blank electrochemical measurements were made on the supporting electrolyte for all bulk electrolysis experiments, and have been subtracted from the presented curves.

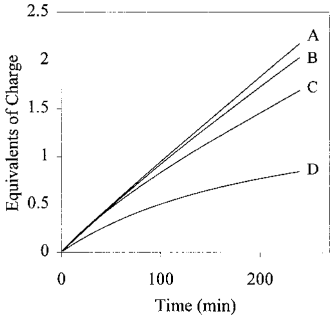


**Figure 1.** Charge−time curves. Controlled potential electrolysis of (A) [Co(*trans*-diammac)]$^{3+}$, (B) [Co(*cis*-diammac)]$^{3+}$, (C) [Co(sep)]$^{3+}$, and (D) [Co(diClsar)]$^{3+}$. Conditions: 1 mM, pH 7.0 phosphate buffer, Hg pool, −1 V vs Ag/AgCl.

## Results

The potential of the [Co(*trans*-diammac)]$^{3+/2+}$ couple (−0.75 V vs Ag/AgCl) is the most negative of the compounds studied in this paper, and among the most negative redox potentials known for Co$^{III}$.[35] The [Co(*cis*-diammac)]$^{3+/2+}$ couple is slightly more positive (−0.62 V vs Ag/AgCl). Both complexes are chemically reversible on the voltammetric time scale in neutral aqueous solution, as evident by no decrease in $i_a/i_c$ from unity at all measured scan rates. The heterogeneous kinetics of the [Co(*trans*-diammac)]$^{3+/2+}$ couple are quasi-reversible on glassy carbon, and simulation of peak separations gave a heterogeneous rate constant on glassy carbon of 0.18 cm s$^{-1}$ (pH 7, 0.1 M phosphate buffer). The heterogeneous electron-transfer rate on a Hg drop working electrode is estimated to be an order of magnitude faster under the same conditions. The faster kinetics on Hg is consistent with similar measurements on macrobicyclic Co$^{III/II}$ cage compounds, which also exhibit this effect.[36]

Bulk electrolysis of a number of hexaaminecobalt(III) complexes were performed in pH 7.0 phosphate buffer (Hg cathode, −1 V vs Ag/AgCl). It is seen in Figure 1, the charge−time curve for these experiments, that the amount of charge passed by both [Co(*trans*-diammac)]$^{3+}$ (A) and [Co(*cis*-diammac)]$^{3+}$ (B) is more than 1 equiv, so the Co$^{II}$ complexes formed at the cathode are being regenerated to their parent Co$^{III}$ complex. The steady-state current was shown over a range of experiments to vary, and was dependent on the stirring efficiency of the mercury pool. The compounds [Co(*cis*-diammac)]$^{3+}$ and [Co(*trans*-diammac)]$^{3+}$ show similar catalytic activity, and electrolysis has been carried out for up to 12 h, resulting in more than 10 equiv of charge being passed. Essential to the passing of more than 1 equiv of charge is the presence of buffer as a supporting electrolyte to maintain constant pH. Bulk electrolysis of an unbuffered 1 mM solution of [Co(*trans*-diammac)]$^{3+}$ at pH 4.5 (Hg pool, −1.0 V vs Ag/AgCl, 0.1 M NaClO$_4$) resulted in the passage of approximately 1 equiv of charge, and the final solution pH was 9, indicating that H$^+$ ions had been consumed during the experiment.

To demonstrate that H$_2$ was indeed the product of this reaction, a manometer was attached to the air-tight cell during electrolysis of a deoxygenated, buffered (pH 7.0) solution of 25 mM [Co(*trans*-diammac)]$^{3+}$, and the results are given in the Supporting Information. An interesting feature of the graph is

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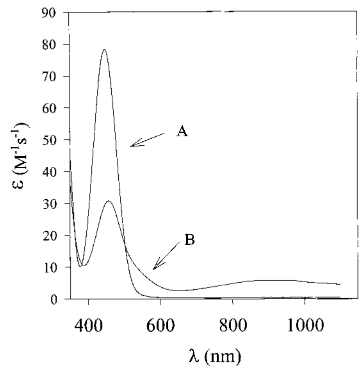

**Figure 2.** Electronic spectra of (A) $[Co(\textit{trans}\text{-diammac})]^{3+}$ and (B) $[Co(\textit{trans}\text{-diammac})]^{2+}$.

that the initial rate of $H_2$ production is small, but this increases, ultimately to a constant level after about 45 min.

Identical controlled potential electrolysis experiments were performed on the two macrobicyclic cage compounds $[Co(sep)]^{3+}$ and $[Co(diClsar)]^{3+}$; the results are also presented in Figure 1. It is seen that $[Co(sep)]^{3+}$ (C) has catalytic activity, whereas the $[Co(diClsar)]^{3+}$ (D) complex is inactive. This concurs with the results of Grätzel and co-workers,[33] who performed this same experiment for $[Co(sep)]^{3+}$ and also identified $H_2$ to be the product of the $[Co(sep)]^{2+}$ oxidation.

The effect of pH and supporting electrolyte on the electrolysis of $[Co(\textit{trans}\text{-diammac})]^{3+}$ was examined, and it was found that using pH 5.8 phosphate buffer resulted in the passage of 1 equiv of charge and an exponential decrease in current to the background level. Cyclic voltammetric measurements revealed the instability of the $Co^{II}$ species at pH 5.8 in phosphate or citrate buffer, with both the $[Co(\textit{trans}\text{-diammac})]^{3+/2+}$ and $[Co(\textit{cis}\text{-diammac})]^{3+/2+}$ couples becoming irreversible in a manner consistent with an EC mechanism.[41,42] This is due to the protonation of one of the pendant amines concomitant with coordination of a buffer anion. However, the electrochemistry is reversible at pH 5.8 in aqueous $NaClO_4$ solution, as the $ClO_4^-$ anion is an uncompetitive ligand.

To test the importance of Hg in the electrocatalytic process, controlled potential electrolysis at the same potential (−1 V vs Ag/AgCl) was performed on $[Co(\textit{trans}\text{-diammac})]^{3+}$ using a reticulated vitreous carbon (RVC) cathode. The result was that the current decayed exponentially, passing 1 equiv of charge at all pH values; i.e., there is no regeneration of $[Co(\textit{trans}\text{-diammac})]^{3+}$ from $[Co(\textit{trans}\text{-diammac})]^{2+}$ on this electrode surface. The electronic spectrum of the resulting $[Co(\textit{trans}\text{-diammac})]^{2+}$ solution is shown in Figure 2, with the initial spectrum of $[Co(\textit{trans}\text{-diammac})]^{3+}$. The $Co^{II}$ spectrum is similar to that reported for $[Co(sep)]^{2+}$,[43] which has been found to be a high-spin $d^7$ complex. Aeration resulted in complete regeneration of the $Co^{III}$ complex.

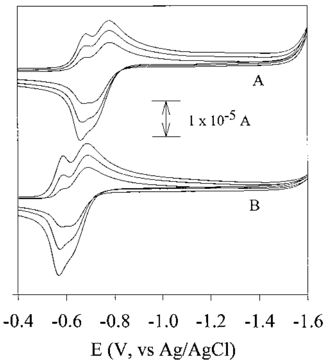

**Figure 3.** Cyclic voltammograms of (A) 1 mM $[Co(\textit{trans}\text{-diammac})]^{3+}$ and (B) 1 mM $[Co(\textit{cis}\text{-diammac})]^{3+}$. Conditions: hanging mercury drop, 0.1 M $NaClO_4$, pH 7, scan rates 1, 2, and 3 V/s.

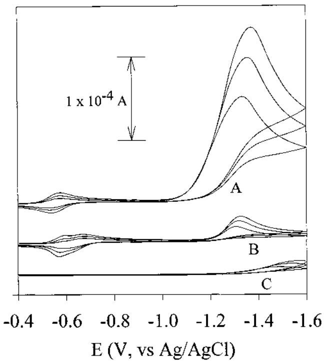

**Figure 4.** Cyclic voltammograms of 1 mM $[Co(\textit{cis}\text{-diammac})]^{3+}$ at (A) pH 2 and (B) pH 3 at scan rates of 1, 2, and 3 V/s and (C) a blank, pH 3. Conditions: hanging mercury drop, 0.1 M $NaClO_4$ + $HClO_4$.

Figure 3 shows the cyclic voltammograms of $[Co(\textit{trans}\text{-diammac})]^{3+}$ and $[Co(\textit{cis}\text{-diammac})]^{3+}$ in 0.1 M $NaClO_4$ at pH 7. A significant feature is strong adsorption. At pH 7 there are clearly two cathodic peaks present, the diffusion-limited reduction of the $Co^{III}$ complex and the more positive cathodic response due to adsorption. This diffusion limited response increases linearly with the bulk concentration of complex as expected. Chronocoulometry was used to study the adsorption of both the $Co^{III}$ and $Co^{II}$ complexes of *trans*-diammac.[44−46] Both forms of the complex were found to adsorb and so it was necessary to estimate the background double-layer charging with a blank solution, and quantify the adsorbed species with a single-step experiment. The results are presented in the Supporting Information, which show the $Co^{II}$ complex to be more strongly adsorbed than the $Co^{III}$ complex. The more positive peaks in the voltammograms are thus due to the reduction of adsorbed $[Co(\textit{trans}\text{-diammac})]^{3+}{}_{ads}$ to a more strongly adsorbed $[Co(\textit{trans}\text{-diammac})]^{2+}{}_{ads}$ complex.[47,48] The diffusion-limited wave gives a linear plot for $i_{pc}$ vs $v^{1/2}$ ($v$ is the sweep rate) whereas for the more positive (adsorption) response $i_{pc}$ is linear with respect to $v$ (Supporting Information).

The voltammograms of $[Co(\textit{cis}\text{-diammac})]^{3+}$ below pH 3.5 show the emergence of a new cathodic peak at −1.3 V. This peak becomes larger when the pH is lowered further, confirming that it is due to proton reduction. Figure 4 shows the voltammograms for 1 mM $[Co(\textit{cis}\text{-diammac})]^{3+}$ at pH 3.0 and 2.0, which are compared to the blank perchloric acid/sodium perchlorate solution recorded at pH 3.0. An increase in the scan rate has a negligible effect on the potential of the $H^+$ reduction peaks in the presence of $[Co(\textit{cis}\text{-diammac})]^{3+}$, indicating that the kinetics of $H^+$ reduction in the presence of the complex are facile. A similar behavior is observed for $[Co(\textit{trans}\text{-diammac})]^{3+}$ at pH below 3.5 (Supporting Information). However, below pH 3.0 the $[Co(\textit{trans}\text{-diammac})]^{3+/2+}$ couple becomes irreversible, indicating that the reduced trans complex is more susceptible to protonation than the reduced cis complex.

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We propose that the explanation for the cathodic waves at −1.3 V vs Ag/AgCl is that the adsorbed $[Co(\textit{cis}\text{-diammac})]^{2+}{}_{ads}$ or $[Co(\textit{trans}\text{-diammac})]^{2+}{}_{ads}$ complexes mediate electron transfer between the electrode and protons at this potential. The process is confined to the surface of the electrode and does not occur in solution; otherwise a catalytic peak would be observed closer to the $Co^{III/II}$ couple. To confirm this, a sample was taken from a Hg pool bulk electrolysis experiment after complete reduction to $[Co(\textit{trans}\text{-diammac})]^{2+}$ had been achieved. In an air-tight cell no reoxidation of $[Co(\textit{trans}\text{-diammac})]^{2+}$ was apparent even after several days, indicating that the catalytic process is not homogeneous. The addition of Hg to this solution also did not increase the rate of oxidation, which indicates that the catalytic process does not occur on the surface of mercury in an open circuit.

## Discussion

The evidence presented above indicates that the adsorbed complexes $[Co(\textit{trans}\text{-diammac})]^{2+}{}_{ads}$, $[Co(\textit{cis}\text{-diammac})]^{2+}{}_{ads}$, and $[Co(sep)]^{2+}{}_{ads}$ mediate electron transfer between the electrode and protons to catalytically evolve dihydrogen. The parent $Co^{III}$ complex is regenerated by proton reduction. However, the reduction of protons is not a homogeneous process, as it does not occur in solution, even if mercury is present. The existence of a polarized electrode is necessary.

The $H^+$ reduction peaks are somewhat negative of that of the $Co^{III/II}$ couple. This raises the possibility that a $Co^I$ complex may be responsible for the catalytic effect, through oxidative addition of a proton to form a hydridocobalt(III) complex, which then undergoes protonation to liberate $H_2$. A number of $Co^I$ complexes have been observed in catalytic cycles, including model vitamin $B_{12}$ complexes, where a $Co^{III}$ complex is reduced to $Co^I$ and then undergoes oxidative addition.[49−55] A $Co^I$ intermediate has been proposed for the complex of an oximate ligand that catalyzes $H_2$ evolution in acidic solution containing $Cr^{2+}$.[56]

We have been unable to identify a $Co^{II/I}$ or $Co^{II/0}$ response for our macrocyclic complexes in aqueous solution. In an attempt to locate the $[Co(\textit{cis}\text{-diammac})]^{2+/+}$ couple in nonaqueous (DMF) solution, we only found an irreversible $Co^{II/0}$ response ca. 1.5 V negative of the $Co^{III/II}$ wave (Supporting Information). If the switching potential is set to just negative of that of the $Co^{III/II}$ couple, then the response is totally reversible, which mirrors the aqueous electrochemistry. However, when the switching potential is taken to a value past the $Co^{II/0}$ wave, then both responses are irreversible, which may be attributed to reduction of $[Co(\textit{cis}\text{-diammac})]^{2+}$ to a $Co^0$ species that dissociates, and the reversibility of the $Co^{III/II}$ couple is lost as a consequence. Therefore, $Co^I$ complexes cannot play a role in the present catalytic chemistry, as this oxidation state is inaccessible in water. Moreover, geometric constraints of the encapsulating macrocycles *trans*-diammac, *cis*-diammac, and sep prohibit additional coordination of a hydrido ligand.

Therefore, we conclude that a $Co^{II}$ complex must be the catalytically active species in the presence of a polarized electrode. The bulk electrolysis experiments did show that −1 V vs Ag/AgCl is a sufficiently negative potential for the process to occur, but it is much faster at −1.3 V vs Ag/AgCl, and the voltammetry concurs with this. The actual mechanism is difficult to elucidate. The strong adsorption of $[Co(\textit{trans}\text{-diammac})]^{2+}{}_{ads}$ to the surface of mercury dictates that an inner sphere mechanism must be responsible, as it has been shown that catalysis on the surface of an electrode cannot proceed by an outer sphere mechanism.[57] Oxidative addition of a proton to the $Co^{II}$ complex is not possible as it would have to proceed through an inaccessible cobalt(IV) hydrido intermediate. Moreover, the $Co^{II}$ complexes in this work are encapsulated, and so they are unable to accommodate an additional ligand. For example, $[Co(sep)]^{2+}$ is kinetically inert, and optically pure samples do not racemize in solution.[39] To explain the observed electrocatalytic activity incorporating an inner sphere mechanism, we propose that the protons attached to the coordinated amines are eliminated as $H^{\bullet}$, leaving the deprotonated $Co^{III}$ complex $[Co^{III}(L-H)]^{3+}$ as the product, which undergoes rapid protonation to regenerate the starting complex:

$$[Co^{III}L]^{3+} + e^- \rightleftharpoons [Co^{II}L]_{ads}{}^{2+}$$

$$[Co^{II}L]_{ads}{}^{2+} \rightarrow [Co^{III}(L-H)]^{2+} + H^{\bullet}$$

$$[Co^{III}(L-H)]^{2+} + H^+ \rightarrow [Co^{III}L]^{3+}$$

Platinum(IV) cages of diAMsar (1,8-diamino-3,6,10,13,16,19-hexaazabicyclo[6.6.6]eicosane) have been proposed to undergo a similar process at an electrode surface.[58]

## Conclusions

The present study has shown that the pendent arm macrocyclic hexaaminecobalt(III) complexes show characteristics similar to those of the extensively studied Co cage compounds.[36] The increased catalytic activity described here may be attributed to the more negative redox potential of our systems:

$$[Co(\textit{trans}\text{-diammac})]^{3+/2+}: \quad E_{1/2} = -0.75 \text{ V (vs Ag/AgCl)}$$

$$[Co(\textit{cis}\text{-diammac})]^{3+/2+}: \quad E_{1/2} = -0.62 \text{ V (vs Ag/AgCl)}$$

$$[Co(sep)]^{3+/2+}: \quad E_{1/2} = -0.51 \text{ V (vs Ag/AgCl)}^{36}$$

$$[Co(diClsar)]^{3+/2+} \quad E_{1/2} = -0.39 \text{ V (vs Ag/AgCl)}^{36}$$

$[Co(diClsar)]^{3+/2+}$ has the least negative couple of the four compounds tested, explaining its inactivity. The more negative potentials of the other compounds bring the potential of the $Co^{III/II}$ couple closer to the $H_2$ evolution potential at the bare electrode.

The instability of the $Co^{II}$ species at low pH and relatively large potential required to initiate the electrocatalytic process limit the usefulness of these systems for practical applications of hydrogen generation from water. However, as has been seen with the cobalt hexaamine cages,[33] the rapid electron-transfer characteristics and stability in two oxidation states may allow

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these species to find useful applications as electron relay agents in other systems, such as the photoreduction of water.

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**Supporting Information Available:** Graphs of bulk electrolysis steady-state currents (Figure S1), $H_2$ evolution with time (Figure S2), cyclic voltammograms of [Co(*trans*-diammac)]$^{3+}$ in pH 6.0 and 6.4 phosphate buffer (Figure S3), Anson plots for [Co(*trans*-diammac)]$^{3+}$ (Figure S4), cyclic voltammograms of [Co(*trans*-diammac)]$^{3+}$ at pH 2.0 and 3.0 (aqueous solution) (Figure S5), cyclic voltammograms of [Co(*trans*-diammac)]$^{3+}$ in DMF (Figure S6), plots of $i_{pc}$ vs $v^{1/2}$ for and $i_{pc}$ vs $v$ for [Co(*cis*-diammac)]$^{3+}$ at pH 7 (Figure S7). This material is available free of charge via the Internet at http://pubs.acs.org.

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