

# Ru=O complexes as catalysts for oxidative transformations, including the oxidation of water to molecular dioxygen

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## Abstract

This paper presents a short review related to the chemistry of the Ru=O group with data extracted from recent reports described in the literature by the authors of the present review and others. It was presented as an oral contribution to the 2005-Adhoc meeting held in Köln, Germany. The main thermodynamic characteristics of mononuclear complexes containing the Ru=O group are described and the effects produced by different type of electronic perturbations are analyzed through the ligands. Furthermore, an example of heterogenization of a Ru=O complex through a polypyrrol conductive polymer on a graphite electrode and its consequences are also described. Finally a description of complexes bearing two Ru=O groups is carried out with special attention to those complexes that in their higher oxidation states are capable of oxidizing water to molecular dioxygen.

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## 1. Introduction

Ruthenium polypyridyl complexes have been extensively studied over the years because they enjoy a combination of unique chemical, electrochemical and photochemical properties [1] that has allowed to explore a wide variety of fields including photochemistry and photophysics [2], bioinorganics [3] and catalysis [4].

From a catalytic viewpoint Ru complexes have been shown to produce an extensive variety of transformations including: hydrogenation of double bonds, oxidation of organic substrates, isomerization reactions, nucleophilic addition to multiple bonds, carbon–carbon bond formation, CO<sub>2</sub> reduction, etc. [4a]. In the present paper we will describe the thermodynamic and reactivity properties of Ru complexes containing one and two Ru=O groups.

## 2. Results and discussion

### 2.1. Complexes containing one Ru=O group

Over the last two decades a large body of ruthenium polypyridyl complexes containing the aqua ligand directly bonded to the metal has emerged [5]. The [Ru(trpy)(bpy)(H<sub>2</sub>O)]<sup>2+</sup> (trpy = 2,2':6',2''-terpyridine and bpy = 2,2'-bipyridine) described by Meyer and co-workers [5a] constitutes a paradigm of this type of complexes both from a structural and a reactivity viewpoint (the structure of the ligands discussed in the present paper are presented in Chart 1). The higher oxidation states of this type of complexes are active catalysts for a variety of oxidative reactions such as the oxidation of alkenes to epoxides [6], sulfides to sulfoxides [7], phosphine to phosphine oxides [8], alcohols to aldehydes [9] and even saturated alkanes to alcohols [10]. Furthermore, from a bioinorganic perspective, they have also been shown to be able to selectively bind and cleave DNA molecules [11].

From a mechanistic perspective, it has been shown that the Ru=O group can oxidize substrates through a variety of reaction

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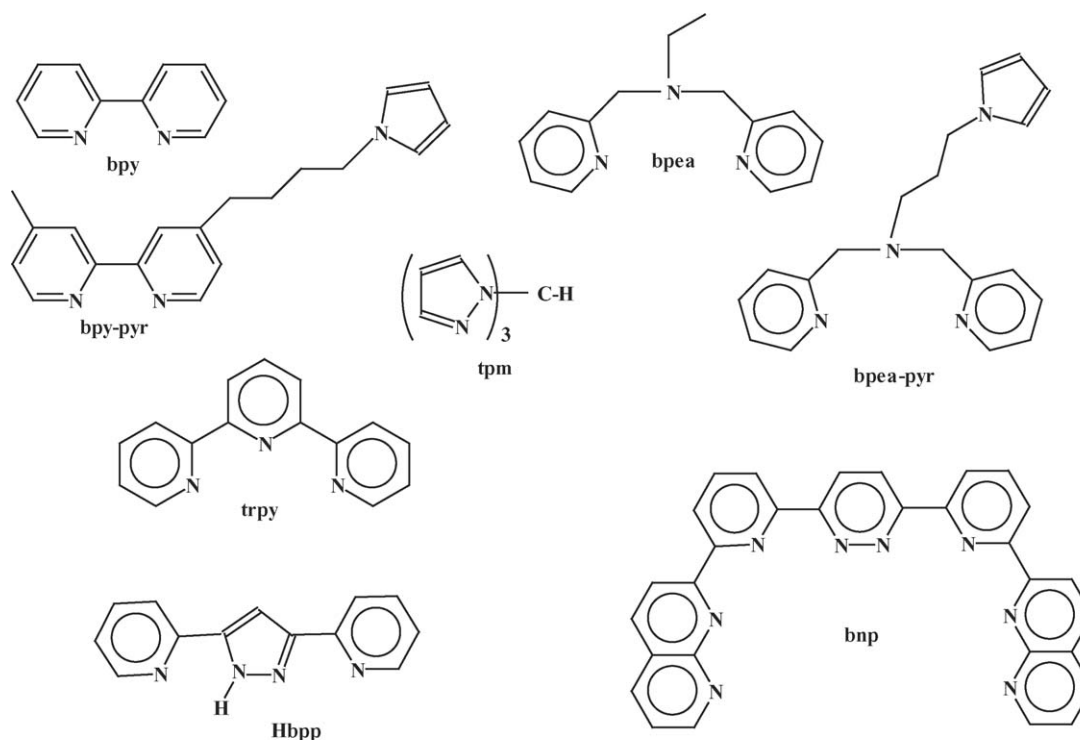
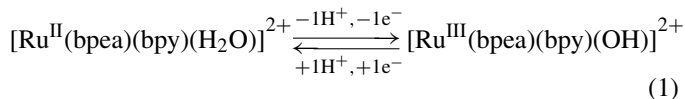


Chart 1. The ligands.

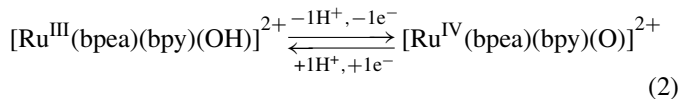
pathways. Those pathways depend on the oxidized substrate and include: outer sphere electron transfer, H-atom transfer, hydride transfer and oxygen atom transfer [1d].

### 2.1.1. Thermodynamic properties

The Ru(II)–H<sub>2</sub>O complexes are of interest because their corresponding higher oxidation states can be reached within a relatively narrow potential range by sequential electron and proton loss, as shown in the Eqs. (1) and (2) for [Ru<sup>II</sup>(bpea)(bpy)(H<sub>2</sub>O)]<sup>2+</sup> (bpea is the tridentate ligand *N,N*-bis(2-pyridylmethyl)ethylamine) [4c]

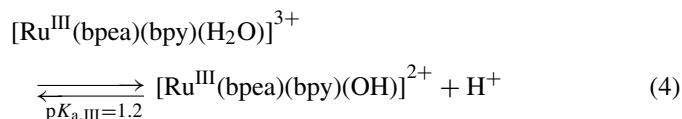
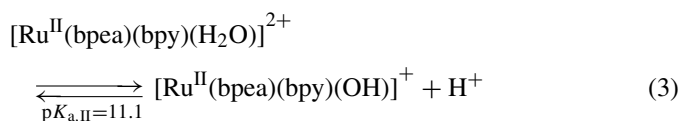


$$E_{1/2}(\text{Ru}^{\text{III/II}} \text{ at pH } 7) = 0.34 \text{ V versus SSCE}$$



$$E_{1/2}(\text{Ru}^{\text{IV/III}} \text{ at pH } 7) = 0.46 \text{ V versus SSCE}$$

The Ru–OH<sub>2</sub> group is also of interest because of the oxidation state dependence of its acid–base properties as shown in Eqs. (3) and (4),



All the thermodynamic properties are neatly represented in the corresponding Pourbaix diagram as shown in Fig. 1 for [Ru<sup>II</sup>(bpea)(bpy)(H<sub>2</sub>O)]<sup>2+</sup>. Representative equations can be extracted from the diagram as shown in Fig. 2, for the same complex.

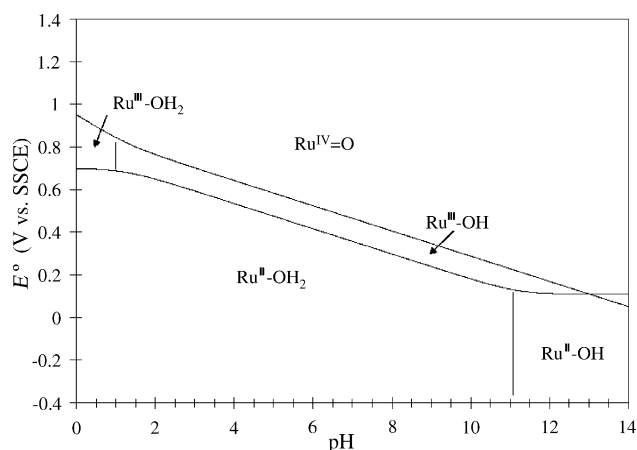


Fig. 1.  $E_{1/2}$  vs. pH or Pourbaix diagram of [Ru(bpea)(bpy)(H<sub>2</sub>O)]<sup>2+</sup>. The pH-potential regions of stability for the various oxidation states and their dominant proton compositions are indicated by using abbreviations such as Ru<sup>II</sup>OH<sub>2</sub>, for example for [Ru<sup>II</sup>(bpea)(bpy)(H<sub>2</sub>O)]<sup>2+</sup>. The  $\text{p}K_{\text{a}}$  values are shown by the vertical solid lines in the various  $E$ -pH regions.

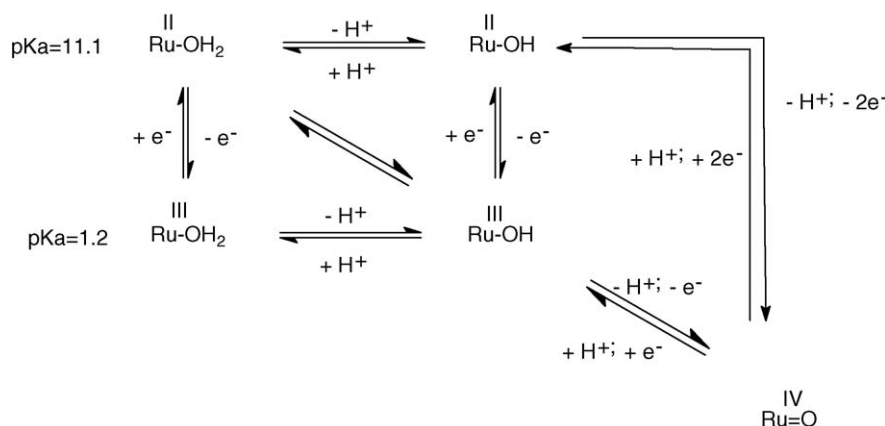


Fig. 2. Equations showing redox couples and their protonation states for species derived from  $[\text{Ru}(\text{bpea})(\text{bpy})(\text{H}_2\text{O})]^{2+}$ .

### 2.1.2. Electronic perturbations

The relatively easy access of the  $\text{Ru}^{\text{IV}}=\text{O}$  high oxidation state (0.46 V at pH 7) is due to the  $\sigma$ - and  $\pi$ -donating ability of the oxo group directly bonded to the Ru metal center. The other five positions available for the Ru metal center are used by ancillary ligands that in the catalytic oxidative processes act mainly as spectator ligands. Those ligands, however, can be used to exert both electronic and steric perturbations and thus they can fine-tune the performance of the  $\text{Ru}=\text{O}$  group (Table 1).

A challenging aspect associated with the chemistry of the  $\text{Ru}-\text{H}_2\text{O}$  type of complexes is the understanding of how electronic factors transmitted by the ligands can influence the stability of the different oxidation states and as a consequence their reactivity.

**2.1.2.1. Remote electronic perturbation.** In a general manner electron donor and electron withdrawing groups are expected to decrease and increase the redox potentials of a given couple, respectively. However, at the moment there is no way one can predict the degree of influence of an electron perturbing group to two successive couples.

An example of this type of perturbation is reported in [12] with the family of complexes  $[\text{Ru}(\text{tpm})(4,4'\text{-X}_2\text{-bpy})(\text{H}_2\text{O})]^{2+}$  (tpm is the tridentate facial ligand tris(1-pyrazolyl)methane and  $4,4'\text{-X}_2\text{-bpy}$  is the  $4,4'$  disubstituted bpy with X being electron donor (e-donor) and electron withdrawing (e-withdrawing) groups such as  $-\text{NH}_2$  or  $-\text{NO}_2$ ). In this family of complexes

the electronic perturbation is thus exerted through the bpy ligand. In this particular case it turns out that the e-donor and e-withdrawing groups strongly influence the III/II redox couple whereas the IV/III is much less affected. Therefore, e-donor produce an enlargement of the zone of stability of oxidation state III whereas e-withdrawing produce just the opposite.

**2.1.2.2. Direct electronic perturbation.** The electronic structure of the Ru metal center can also be directly perturbed when bonded directly to strong  $\sigma$ -donor type of ligand such as acetylacetonato (acac) or with  $\pi$ -acceptors such as tertiary phosphines. For such purpose a family of Ru complexes with general formula  $[\text{Ru}(\text{trpy})(\text{X-X})(\text{H}_2\text{O})]^{n+}$  ( $\text{X-X} = \text{acac}$ ,  $n = +$ ;  $\text{X-X} = \text{bpy}$ ,  $n = 2+$ ;  $\text{X-X} = 1,2\text{-bis}(\text{diphenylphosphine})\text{ethene}$  (dppene),  $n = 2+$ ) are examined [13]. As in the previous section the acac ligand strongly affects the III/II couple whereas the IV/III is much less affected. However, and in sharp contrast with the previous case, with the phosphine ligand the IV/III couple is now more affected than the III/II. As a consequence of this, for this family of complexes, the electronic perturbations always produce an enhancement of the zone of stability of the oxidation state III.

### 2.1.3. Heterogenization of complexes with the $\text{Ru}=\text{O}$ group

Another important aspect related to this family of complexes is its heterogenization, given the intrinsic advantages of heterogeneous processes versus homogeneous. Those advantages include ease of catalyst separation from the formed products

Table 1  
Electrochemical data and  $\text{p}K_{\text{a}}$  for the complexes described in the paper

Complex	$E_{1/2}$ (V) vs. SSCE			$\Delta E_{1/2}^{\text{a}}$	$\text{p}K_{\text{a,II}}^{\text{b}}$	$\text{p}K_{\text{a,III}}^{\text{b}}$
	IV/III	III/II	IV/II			
$[\text{Ru}(\text{bpea})(\text{bpy})(\text{OH}_2)]^{2+}$	0.46	0.34	0.40	120	11.1	1.2
$[\text{Ru}(\text{tpm})(\text{bpy})(\text{OH}_2)]^{2+}$	0.71	0.40	0.55	310	10.8	1.9
$[\text{Ru}(\text{tpm})(4,4'\text{-(NH}_2)_2\text{-bpy})(\text{OH}_2)]^{2+}$	0.59	0.21	0.40	380	11.4	3.5
$[\text{Ru}(\text{tpm})(4,4'\text{-(NO}_2)_2\text{-bpy})(\text{OH}_2)]^{2+}$	0.75	0.56	0.65	190	8.7	1.0
$[\text{Ru}(\text{trpy})(\text{bpy})(\text{OH}_2)]^{2+}$	0.62	0.49	0.56	130	9.7	1.7
$[\text{Ru}(\text{trpy})(\text{acac})(\text{OH}_2)]^+$	0.56	0.19	0.38	370	11.2	5.2
$[\text{Ru}(\text{trpy})(\text{dppene})(\text{OH}_2)]^{2+}$	1.53	1.17	1.35	360	–	–

<sup>a</sup>  $\Delta E_{1/2} = E_{1/2}(\text{IV/III}) - E_{1/2}(\text{III/II})$  in mV.

<sup>b</sup>  $\text{p}K_{\text{a,II}}$  and  $\text{p}K_{\text{a,III}}$  represent  $\text{p}K_{\text{a}}$  for the  $\text{Ru}^{\text{II}}\text{-OH}_2$  and  $\text{Ru}^{\text{III}}\text{-OH}_2$  species, respectively.

together with dramatic minimization of inter-catalyst deactivation due to the absence of diffusion of the anchored catalyst. Furthermore, in the particular case of electrooxidations, the possibility of using conductive polymer supports allows to design modified electrodes with high catalyst concentrations at the surface of the electrode where electron trafficking takes place.

Several techniques have been developed for the attachment of ruthenium electrocatalysts into electrode surfaces. Techniques based on anodic electropolymerization of pyrrole-substituted ruthenium complexes are very convenient methods to firmly attach such catalysts onto the electrode. The resulting modified electrodes are found to be active and selective catalysts for oxidation of a variety of organic substrates including alcohols [14]. The kinetic of the catalysis is generally slower with films compared to bulk solution as a consequence of the slowness of the access to the high oxidation state of the complex and of the chemical reactions coupled with the electron transfer in films. However, the stability of catalyst is dramatically improved in films.

The  $[\text{Ru}(\text{bpea})(\text{bpy})(\text{O})]^{2+}$  has been shown to behave as an excellent homogeneous catalyst with regard to the oxidation of benzyl alcohol [4c]. This behaviour prompted us to design pyrrolic monomers that would allow to polymerize the Ru center without significantly modifying its intrinsic steric and electronic properties, thus allowing a fair comparison of homogeneous versus heterogeneous catalysis with practically the same active center. For this purpose we prepared surrogate  $[\text{Ru}(\text{bpea})(\text{bpy})(\text{H}_2\text{O})]^{2+}$  complexes with similar ligands but substituted by a pyrrol group noted  $\text{bpea-pyr}$  and  $\text{bpy-pyr}$ . In general we found that the performance of the heterogenized systems increased the number of metal cycles by more than two orders of magnitude, manifesting the increased robustness of the new materials.

## 2.2. Complexes containing two Ru=O

As shown in the previous section mono-aqua complexes of Ru can lose two protons and two electrons and generate the Ru=O active catalyst. Meyer's group has shown that mononuclear bis-aqua complexes of Ru can lose up to four protons and four electrons and generate the corresponding  $\text{Ru}^{\text{VI}}(\text{O})_2$  complexes. This is actually the same number of protons and electrons that are lost in the oxidation of water to molecular dioxygen, performed by the oxygen evolving center (OEC) of the green plants photosystem II (PSII).



However, in this case besides the loosing of the mentioned electrons and protons an oxygen–oxygen bond is not formed and thus no molecular dioxygen is generated. To be able to generate molecular oxygen the present literature indicates that a dinuclear type of complex with a terminal oxo group in each metal is needed.

The reaction shown in Eq. (5) is a thermodynamically demanding reaction since  $E^\circ = 1.23 \text{ V}$  versus NHE at pH 0. On the other hand, it is of tremendous molecular complexity

from a mechanistic perspective, since it involves the oxidation of water by  $4\text{H}^+$  and  $4\text{e}^-$  with concomitant formation of an oxygen–oxygen bond. This is an important reaction to be modeled since efficient models can lead to a first step towards creating a clean renewable energy source. Recently, an X-ray structure of PSII structure from the cyanobacterium “*Thermosynechococcus elongatus*” (MW = 650 kDa) at 3.5 Å resolution [15] has allowed to identify the structure of OEC-PSII with great precision. In this structure it is shown that the OEC-PSII consists of a tetranuclear Mn complex where the metal centers are linked to one another through oxo bridges. This unique structure has no parallel in the laboratories at the moment and thus synthetic structural models are being sought.

### 2.2.1. Dinuclear complexes with an oxo bridging ligand

From a reactivity point of view there are very few well defined molecules that are capable of oxidizing water to molecular dioxygen in homogeneous phase in water and in the absence of light, as it happens in the OEC-PSII. A number of Ru complexes containing the Ru–O–Ru motif have been described, with the blue dimer (the *cis,cis*- $[\{\text{Ru}(\text{bpy})_2(\text{H}_2\text{O})\}_2\text{O}]^{4+}$  (bpy is 2,2'-bipyridine)) being its paradigm and whose structure is shown in Fig. 3 [16]. However, in homogeneous phase the turnover numbers for the blue dimer and its surrogates are low and the complex loses its activity mainly due to anation.

### 2.2.2. Dinuclear complexes with no oxo bridging ligands

We have recently presented the first example of a well characterized, from a structural and electrochemical viewpoint, dinuclear Ru complex capable of oxidizing water to  $\text{O}_2$  that does not contain the Ru–O–Ru motif [17]. Instead, two Ru metals have been deliberately placed at close proximity and in an adequate orientation using the dinucleating Hbpp and the meridional trpy ligands as shown in Fig. 4.

The water splitting rate presented by  $[\text{Ru}_2(\text{bpp})(\text{trpy})_2(\text{O})_2]^{3+}$  constitutes one of the highest initial rates reported up to date, although it is about four times slower than that of  $[(\text{NH}_3)_3\text{Ru}(\mu\text{-Cl})_3\text{Ru}(\text{NH}_3)_3]^{2+}$  ( $5.6 \times 10^{-2} \text{ s}^{-1}$ ) reported by

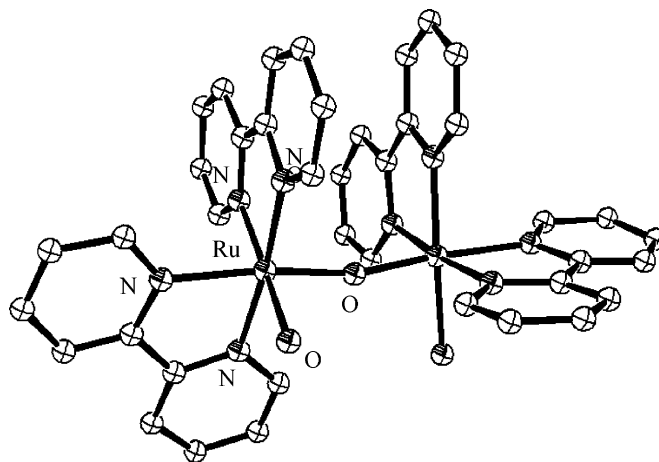


Fig. 3. Structure of the cation *cis,cis*- $[\{\text{Ru}(\text{bpy})_2(\text{H}_2\text{O})\}_2\text{O}]^{4+}$  drawn from data reported in ref. [16]. Labels show the metal center and the atoms involved in the first coordination sphere.

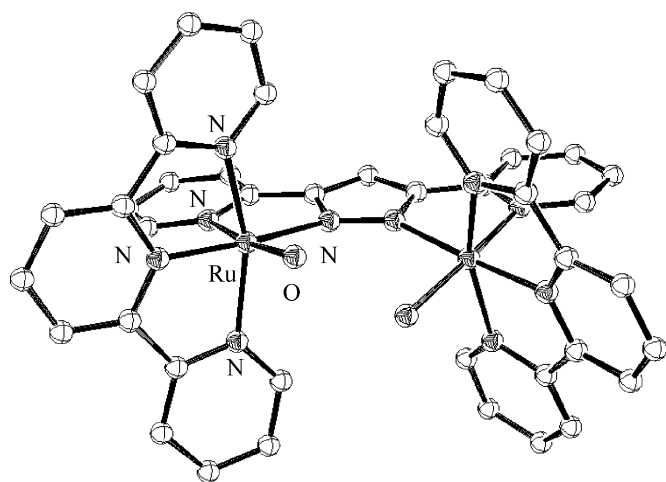


Fig. 4. Structure of the cation  $[Ru_2(bpp)(trpy)_2(OH_2)_2]^{3+}$  drawn from data reported in ref. [17]. Labels show the metal center and the atoms involved in the first coordination sphere.

Kaneko and co-workers [18]. However, the latter system suffers from deactivation processes that generate  $N_2$ , that in turn are responsible for a very narrow range of linear behavior. In sharp contrast the dinuclear complex  $[Ru_2(bpp)(trpy)_2(O)_2]^{3+}$ , has a range of linearity that is more than an order of magnitude higher than that of  $[(NH_3)_3Ru(\mu-Cl)_3Ru(NH_3)_3]^{2+}$ . Thus, it constitutes the most rugged system capable of oxidizing water to molecular oxygen reported up to date.

Mechanistically complex  $[Ru_2(bpp)(trpy)_2(O)_2]^{3+}$ , is also highly interesting since due to the *in, in* configuration of the oxo ligands and the strategic disposition and encumbrance of the trpy ligands, intermolecular oxo–oxo interaction should be negligible and therefore, only the intramolecular pathway for dioxygen formation can operate in this complex.

Very recently Thummel and co-workers [19] have found a new complex that is also capable of performing this reaction using the same principles as in our case, that is, no oxo-bridge and rigidly facing  $Ru=O$  entities using the ligand 3,6-bis-[6'-(1'',8''-naphthyrid-2''-yl)-pyrid-2'-yl]pyridazine (bnp). However, in this case the corresponding  $Ru-OH_2$  precursors have not been characterized.

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