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Ru Complexes That Can Catalytically Oxidize Water to Molecular Dioxygen

Isabel Romero,[†] Montserrat Rodríguez,[†] Cristina Sens,[†] Joaquim Mola,[†] Mohan Rao Kollipara,[‡] Laia Francàs,[‡] Elena Mas-Marza,[§] Lluís Escriche,[‡] and Antoni Llobet*,[‡,§]

Departament de Química, Universitat de Girona, Campus de Montilivi, E-17071 Girona, Spain, Departament de Química, Universitat Autònoma de Barcelona, Cerdanyola del Vallès, E-08193 Barcelona, Spain, and Institute of Chemical Research of Catalonia (ICIQ), Avinguda Països Catalans 16, E-43007 Tarragona, Spain

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The main objective of this review is to give a general overview of the structure, electrochemistry (when available), and catalytic performance of the Ru complexes, which are capable of oxidizing water to molecular dioxygen, and to highlight their more relevant features. The description of the Ru catalysts is mainly divided into complexes that contain a Ru−O−Ru bridging group and those that do not. Finally a few conclusions are drawn from the global description of all of the catalysts presented here, and some guidelines for future catalyst design are given.

1. Introduction

The Noble Laureate Richard Smalley published a paper in 2004[1] in which he affirmed, “If you have enough energy you can solve many of the top ten problems the world is facing such as water, food supplies, poverty and disease.” The prediction for energy demand by the year 2050 is in the range of 30–50 TW,[2] which is more than a 100% increase with regards to what we have consumed in the year 2004. Further, given the increase in the rate of CO_2 production and the catastrophic consequences this increase is producing for our planet,[3] he concludes that the additional energy has to come necessarily from carbon-neutral renewable sources and mainly from solar energy. This subject has also recently been reviewed in an “Inorganic Chemistry Forum”.[4] Nathan S. Lewis and Daniel G. Nocera recently wrote a perspective paper dealing with this subject, in which they also discussed and quantified the increasing demands for energy that our society is facing and further linked our access to energy resources with other issues including “National Security”.[5] According to these authors and others,[6] solving the energy problem is so urgent that it needs to be done within the next 10–20 years, which, from a scientific point of view, is just around the corner.

An attractive and clean energy source to solve this problem could be hydrogen, but while the storage and separation of hydrogen has already been achieved with a certain degree of success,[7] the question of a sustainable hydrogen source still remains to be answered.[8] Nature has been using water and sunlight as a source of energy in its photosynthetic processes for a long time. Oxidation of water to dioxygen is

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* To whom correspondence should be addressed. E-mail: allobet@ iciq.es.
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[‡] Universitat Autònoma de Barcelona.
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the terminal reaction of photosystem II (PSII) in green plants, which takes place at a polynuclear Ca$-$Mn$_4$ complex.

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^- \qquad (1)$$

This reaction is thermodynamically demanding because $E° = 1.23$ V (vs SHE) at pH = 0.0. On the other hand, it is of tremendous molecular complexity from a mechanistic perspective because it involves the oxidation of water by $4H^+$ and $4e^-$ with the formation of an O$-$O bond. It is thus an important reaction to be modeled because efficient low molecular weight models can lead to a first step toward creating a clean renewable energy source. Recently, substantial efforts have been directed at the elucidation of the structure and water oxidation mechanisms that take place at the oxygen-evolving complex (OEC) of PSII,[9–13] constituting fundamental information to inspire future research.

There are very few well-defined molecules that are capable of oxidizing water to dioxygen in a homogeneous phase (HoP) and in the absence of light, as in the OEC-PSII. Only two Mn complexes have been shown to be capable of doing so,[14–16] using water as a solvent, although they are not free of certain controversy and present relatively poor performances.[17] On the other hand, a number of Ru complexes have been described that are much more robust and that will be the focus of the present review. This review will concentrate mainly on Ru complexes that have been molecularly *well characterized* and whose catalytic activity has been tested in a HoP with only key examples in a heterogeneous phase (HeP), including those molecules that have been anchored on solid supports that are complementary to a HoP, and that are of interest to understand the overall chemistry of the catalyst. This review will not deal with water photooxidation processes; it will deal only with water oxidation reactions that take place in the dark, as in the OEC-PSII. A few reviews have partially covered the subject of water oxidation within a broader scope of Ru complexes as oxidative reagents for organic and inorganic substrates.[18] This review is solely devoted to the catalytic oxidation of water to molecular dioxygen.

Finally, the main objective of this review is to give a general overview of the structure and catalytic performance of Ru complexes that are capable of oxidizing water to molecular dioxygen and to highlight their more relevant features. A more in-depth description of the complexes and reactions described are accessible in the given references.

2. General Considerations

Most of the described Ru complexes described that are capable of oxidizing water to molecular dioxygen are based on, or are precursors of, the so-called Ru$-$OH$_2$/Ru$=$O system discovered by Thomas J. Meyer's group about 3 decades ago.[19] The capacity of ruthenium aquopolypyridyl complexes to lose protons and electrons and easily reach higher oxidation states[20] is exemplified by the following equation (L = polypyridine ligand):

$$L_5Ru^{II}{-}OH_2 \underset{-H^+ - e^-}{\overset{-H^+ - e^-}{\rightleftharpoons}} L_5Ru^{III}{-}OH \underset{-H^+ - e^-}{\overset{-H^+ - e^-}{\rightleftharpoons}} L_5Ru^{IV}{=}O \qquad (2)$$

The higher oxidation states are accessible within a narrow potential range mainly because of the σ- and π-donation character of the oxo group. In addition, the simultaneous loss of protons and electrons precludes an otherwise highly destabilized scenario invoking highly charged species. A large amount of literature has emerged related to these types of systems mainly because of the rich oxidative properties of the Ru^{IV}$=$O species. Reaction mechanisms for the oxidation of several substrates by Ru^{IV}$=$O have been established and catalytic oxidation systems described.[21]

Systems containing two Ru$-$OH$_2$ groups accordingly can lose four protons and four electrons, which is exactly what is needed for the oxidation of water to molecular dioxygen, as takes place in the OEC-PSII (see eq 1), together with the formation of an O$-$O bond.

The oxidation of water can take place following multiple reaction pathways, and it is important to bear in mind the thermodynamics associated with those pathways, as presented in Scheme 1. In this review, all redox potentials, unless explicitly mentioned, will be reported versus the SSCE reference electrode because most of the work related to this chemistry has been carried out under these conditions.

The description of the Ru catalysts will be divided into two sections: those complexes that contain a Ru$-$O$-$Ru bridging group and those that do not. The structures presented

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Scheme 1. Thermodynamics of Water Oxidation

Redox couple	$E^{o'}$, V (vs. SSCE)	
	pH = 1.0	pH = 7.0
$OH + 1H^+ + 1e^- \rightarrow H_2O$	2.5	2.15
$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$	1.48	1.13
$HO_2 + 3H^+ + 3e^- \rightarrow 2H_2O$	1.37	1.02
$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$	0.94	0.58

in this review are based on X-ray structures when available and, when X-ray structures are not available, on semiempirical calculations at the ZINDO[22] level performed using the *CAChe* program package.[23] The color codes of the drawings are as follows: C, black; N, blue; O, red; Ru, orange; Zn, yellow; W, brown. All H atoms are omitted.

3. Oxo-Bridging Catalysts

3.1. Blue Dimer. In 1982, Meyer's group reported the synthesis, structure, and electrochemical properties of a dinuclear complex *cis,cis*-$[(bpy)_2(H_2O)Ru(\mu\text{-}O)Ru(H_2O)(bpy)_2]^{4+}$ (**1**; bpy is 2,2′-bypyridine chelating ligand L1 shown in Scheme 2; this scheme shows all of the ligands discussed in this review) that is commonly known as the "blue dimer" ($\lambda_{max} = 637$ nm; $\epsilon = 21\,100$ at pH = 1.0).[24] In this dimer, each metal center contains a $Ru-OH_2$ group in oxidation state III, while the two Ru metals are bridged by an oxo ligand, with the remaining octahedral coordination sites being occupied by bpy ligands, as shown in Figure 1A. The torsion angle between the O atoms of the aquo ligands and the two Ru metals is 65.7°. It is also important to note here that those aquo ligands are cis with regard to the oxo-bridging ligand but that other isomers such as cis,trans and trans,trans could also be obtained.

A thorough thermodynamic picture of the zones of stability of the different oxidation states of the blue dimer can be observed in the Pourbaix diagram, which is presented in Figure 1B. For the blue dimer, lower oxidation states such as III,II undergo reductive cleavage of the Ru−O−Ru bond within the cyclic voltammetry time scale, leading to the corresponding mononuclear complexes. This chemistry is typical for such oxo-bridged compounds[25] and thus is not shown in the Pourbaix diagram.

For the blue dimer, at pH = 1.0 two redox processes are observed. One process at $E°' = 0.79$ V involves the removal of one electron from the III,III oxidation state to give the III,IV oxidation state, whereas the second process involves the removal of three electrons from III,IV to give V,V with $E°' = 1.22$ V. Overall, $E°'$ for the four-electron process V,V to III,III appears at 1.12 V, 180 mV above the thermodynamic value for the oxidation of water to molecular dioxygen at pH = 1.0 ($E°' = 0.94$ V; see Scheme 1).

In the presence of excess Ce^{IV}, the blue dimer is capable of oxidizing water to molecular dioxygen, yielding at least 13.2 turnover (TN) cycles.[26] It is assumed that one of the major handicaps for this catalytic cycle is anation that deactivates the process. The slow step in this process has been shown to be the oxidation of the $Ru^{IV}ORu^{III}$ species to the higher oxidation states responsible for oxygen evolution.

A number of mechanistic studies have been carried out with the blue dimer using ^{18}O-labeled water and catalyst, with rather controversial results. While Meyer's group found a ratio of $^{18}O-^{18}O/^{18}O-^{16}O/^{16}O-^{16}O$ of "0.13:0.64:0.23"[27] for the evolved molecular oxygen, Hurst's group found a ratio of "traces:0.40:0.60"[28] in their experiments, and thus their interpretation of the mechanism is rather different. While a relatively high concentration of $^{18}O-^{18}O$ allows the invoking of an intramolecular interaction such as the one shown in Scheme 3A or a bimolecular Ru−O···O−Ru interaction, its absence obviously denies both. The considerable amount of $^{18}O-^{16}O$ found in both experiments strongly advocates for an intermolecular type of mechanism with solvent–water forming a type of hydroperoxide intermediate that eventually evolves oxygen (Scheme 3B). Finally the presence of $^{16}O-^{16}O$ in both cases indicates a certain degree of exchange during the reaction cycle and/or formation of oxygen with no involvement of the $Ru^V{=}O$ groups. Furthermore, the intermediary oxidation state of the "blue" dimer in this mechanism is also in dispute, and therefore it can also have profound mechanistic consequences.

The elucidation of the reaction mechanisms for this process is intrinsically difficult given the number of species present in the reaction cycle that involve different oxidation states with a different degree of protonation. This problem is further complicated by the difficulty of handling the samples under a strict oxygen-free atmosphere, by the limited solubility of the catalyst in water, and by the coordination of anions (anation) as exemplified in eq 3.

Density functional theory calculations have been carried out to shed some light on the possible reaction mechanisms involved in the formation of oxygen.[29] However, at the

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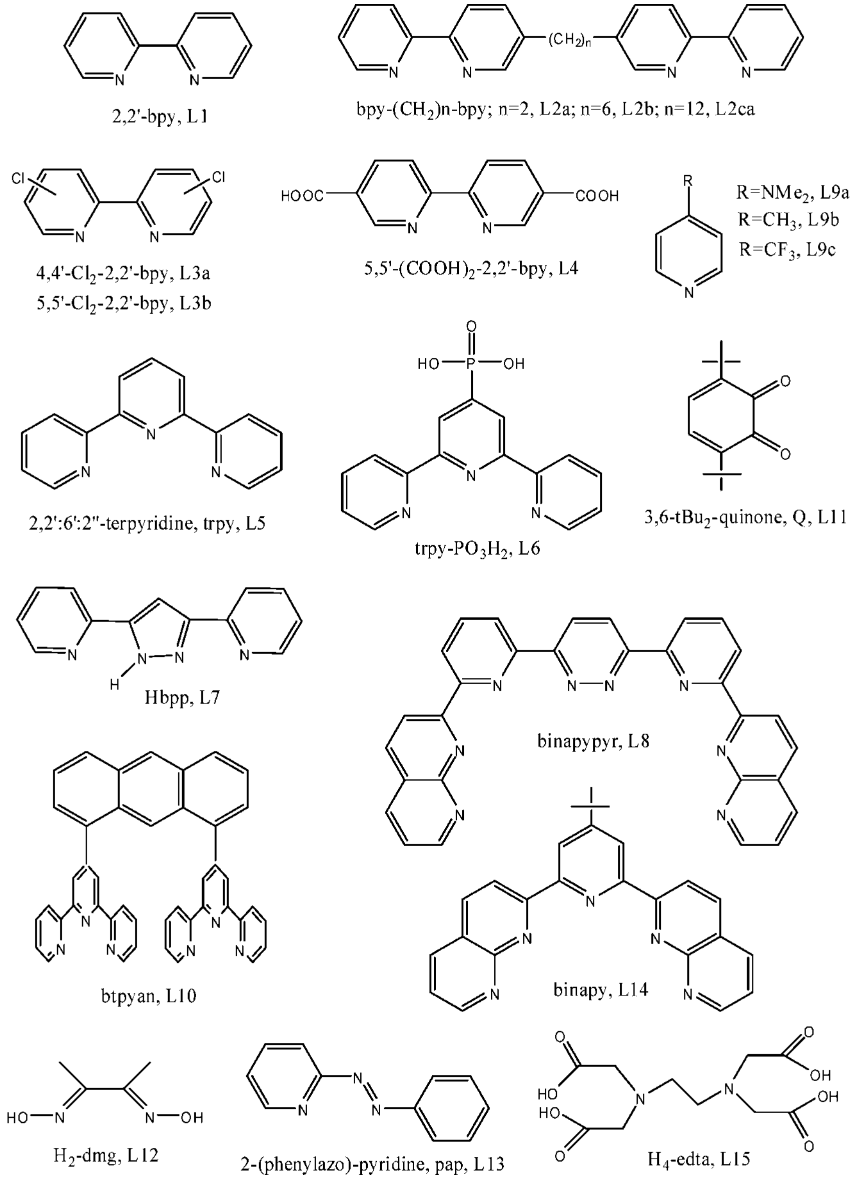
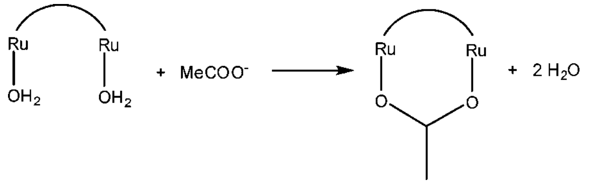
Scheme 2. Ligands Discussed





(3)

available level of theory, the reliability of the results is rather low given (1) the open-shell nature of all of the Ru oxidation states involved, (2) the inherent difficulty in correctly evaluating electron correlation and spin coupling of the metal centers, and (3) the cycling among different oxidation states during the catalytic cycle.[30]

3.2. Blue Dimer in Nafion Membranes. The performance of the blue dimer with regard to the oxidation of water to molecular dioxygen was also studied in a HeP by Yagi and Kaneko[31] using a Nafion polymer as the solid support. The reaction was carried out in water using an excess of Ce^{IV} as the oxidant and was compared to the performance of the blue dimer in a HoP under the same conditions. It was found that in the Nafion membrane the oxygen evolution rates (V_{O_2}) are lower than those in the HoP but the range of linearity in the HeP is an order of magnitude larger than that in the HoP (Figure 2A

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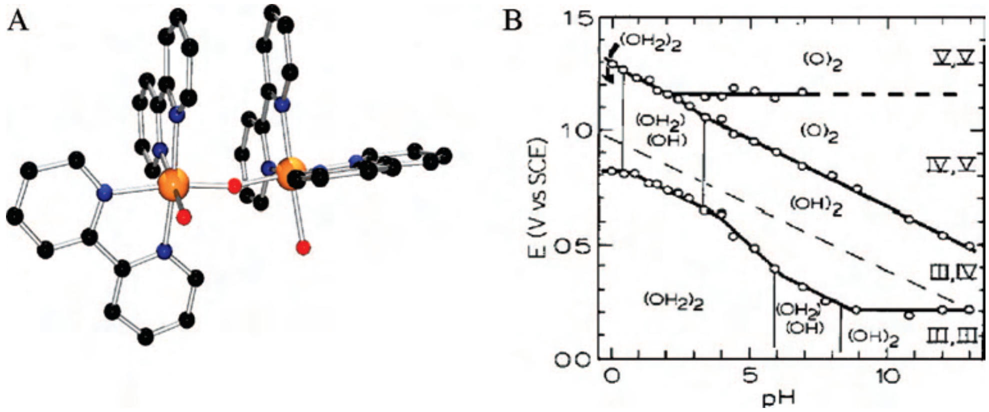


Figure 1. (A) X-ray structure and (B) Pourbaix diagram of **1**. Reprinted with permission from ref 24b. Copyright 1985.

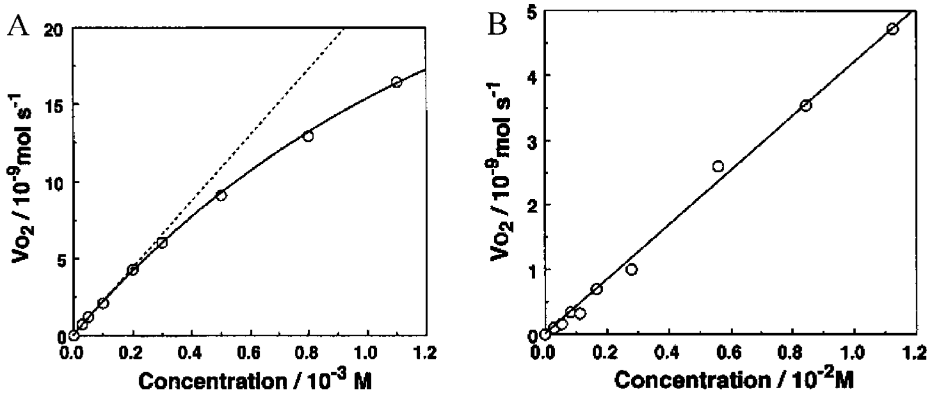
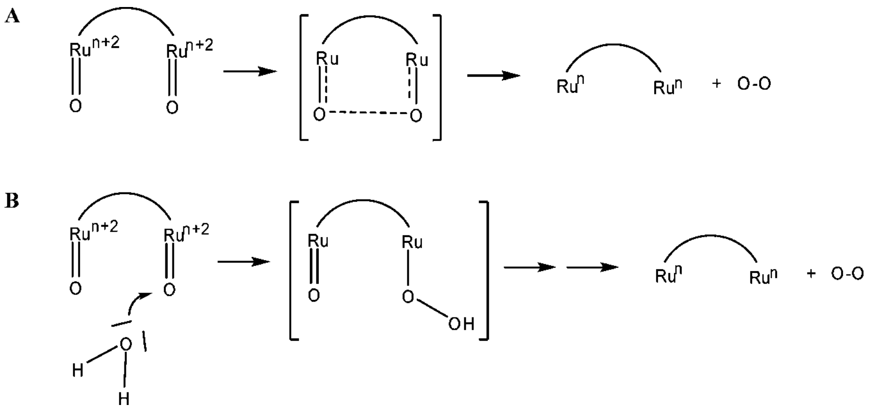


Figure 2. (A) Dependence of the oxygen evolution rate (V_{O2}/mol·s^{-1}) on the complex concentration in aqueous solution. The amount of Ce^{IV} is 3.1 × 10^{-3} mol in 5 mL of water. Reprinted with permission from ref 32b. Copyright 2001, Elsevier. (B) Dependence of the oxygen evolution rate (V_{O2}/mol·s^{-1}) on the catalyst concentration in the HeP in a Nafion membrane. The amount of Ce^{IV} is 3.1 × 10^{-3} mol in 5 mL of water.[30b]

Scheme 3. Potential Mechanistic Pathways for the Formation of Dioxygen, Involving the Ru Metal Centers



for HoP and Figure 2B for HeP). From these results, it is inferred that in the HeP case catalyst deactivation is minimized because of the lack of diffusion that could lead to intermolecular catalyst−catalyst deactivation, that is, the reaction of a Ru═O group of one molecule with the ligand of another one.

Kaneko and co-workers also studied the performance of the dinuclear trichloro-bridged dimer $[(NH_3)_3Ru(\mu\text{-}Cl)_3Ru(NH_3)_3]^{2+}$ (**2**) both in the HoP and in the Nafion membranes,[32] and they claimed that the latter system has one of the largest reported initial rate constants. However, **2** suffers from deactivation processes that generate dinitrogen, which, in turn, is responsible for a very narrow range of linear behavior.

3.3. Blue Dimer Analogues. Elliot and co-workers[33] reported a series of Ru−O−Ru complexes containing alkyl-linked bis-bpy ligands (Scheme 2), *cis*,*cis*-$[(bpy)(H_2O)Ru(\mu\text{-}O)(\mu\text{-}L2a)Ru(H_2O)(bpy)]^{4+}$(**3**), as shown in Figure 3. They claimed that this series of complexes possess a structure similar to the blue dimer, even though their characterization does not include X-ray diffraction analysis, and they isolate **3** as a mixture of different oxidation states. The water oxidation capabilities are found to be similar to those of the blue dimer.

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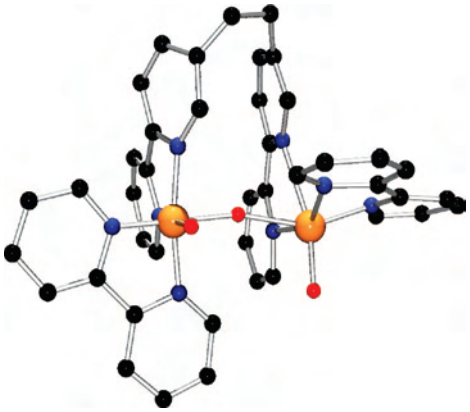

Figure 3. Calculated structure of **3**.

Wong et al. reported the synthesis, electrochemical properties, and characterization of two oxo-bridged dinuclear Ru complexes with structures similar to the blue dimer but with replacement of bpy by 4,4′-dichloro- or 5,5′-dichloro-bpy, *cis*,*cis*-$[(n,n'\text{-Cl}_2\text{-bpy})_2(H_2O)Ru(\mu\text{-O})Ru(H_2O)(n,n'\text{-Cl}_2\text{-bpy})_2]^{4+}$ ($n = n' = 4$, **4**; $n = n' = 5$, **5**).[34] They conclude that both the electrochemistry and the catalytic activities toward the oxidation of water to molecular dioxygen are very similar to those of the blue dimer. However, these Cl-substituted dimers seem to be more stable toward both oxidative and reductive degradation in mild acidic media.

Grätzel and co-workers[35] reported the synthesis and characterization of an oxo-bridged Ru dimer, where the four 2,2′-bpy ligands are replaced by the 2,2′-bipyridyl-5,5′-dicarboxylic acid, L4, *cis*,*cis*-$[(L4)_2(H_2O)Ru(\mu\text{-O})Ru(H_2O)(L4)_2]^{4+}$ (**6**). The electron-withdrawing nature of the carboxylic acid groups has a dramatic effect on the electronic structure of the dimer. For the blue dimer, the IV,III redox potential is 0.79 V, whereas for **6**, the potential is anodically shifted to 1.03 V vs SCE. This renders the oxidation of water to molecular oxygen thermodynamically feasible according to eq 4.

$$4Ru^{III}{-}O{-}Ru^{IV} + 2H_2O \rightarrow 4Ru^{III}{-}O{-}Ru^{III} + O_2 + 4H^+ \qquad (4)$$

In this case, the role of the oxidized dimer **6** is to act four times as a $1e^-$ acceptor, which is rather different from the $4e^-$ acceptor nature of the oxidized blue dimer **1**. Also, Grätzel and co-workers investigated the 2,2′-bipyridyl-4,4′-dicarboxylic acid analogue of the “blue” dimer,[36] which behaved similarly to the 5,5′ isomer.

3.4. trpy Dimer. Another pseudoanalogue of the blue dimer **1** is the “trpy dimer”, shown in Figure 4A, which is generated in an acidic solution from the oxalate derivative. In this dimer, two bpy ligands of the blue dimer are replaced by a meridional trpy ligand and an aquo ligand that are both cis to one another and to the oxo-bridging group, $[(trpy)(H_2O)_2Ru(\mu\text{-O})Ru(H_2O)_2(trpy)]^{4+}$ (**7**).[37] This new arrangement has a pronounced effect on the electronic properties of the Ru centers, with each Ru possessing two aquo ligands such that it could potentially lose $8H^+$ and $8e^-$ with the Ru metals in oxidation state VII. However, as shown in the Pourbaix diagram in Figure 4B, the higher oxidation states that can be reached, as is the case of the blue dimer, are V,V even though the redox potentials of the couples differ significantly. Perhaps the most remarkable feature of this dimer as compared with the blue dimer is the presence of the IV,IV oxidation state over a broad pH range and the fact that this oxidation state does not undergo anation. Oxidation of the IV,IV dimer with Ce^{IV} results in oxygen evolution but in the most favorable case gives only 0.97 TNs, and thus the system is not catalytic. In this case, the oxidation of water to molecular dioxygen is accompanied by dimer decomposition to give the mononuclear complex $[Ru^{VI}(trpy)(O)_2(H_2O)]^{2+}$ (**8**). The driving force for this process is the electronic stabilization associated with the formation of the d^2 *trans*-dioxometal(VI) core.[38] A second deactivation pathway is the formation of a IV,IV′ species, which is attributed to the anated form of the IV,IV species that does not undergo further oxidation with Ce^{IV} and thus drives the process out of the catalytic cycle.[37] As in the case of other oxo-bridged dimers, oxidation states lower than III,III are not stable, undergoing reductive cleavage to the corresponding mononuclear complexes, in this case $[Ru^{II}(trpy)(H_2O)_3]^{2+}$ (**9**).

Very recently, this trpy dimer has been anchored onto solid oxide conductive surfaces, ITO (Sn^{IV}-doped In_2O_3) and FTO (fluorine-doped tin oxide), through the derivatization of the trpy ligand, L6, with the phosphonate group, as shown in Scheme 2. Under these conditions, the system becomes catalytic, giving 3 TNs at pH = 6.[39]

3.5. Ru_2 Centers in a Polyoxometalate (POM) Framework. A dinuclear Ru_2 complex contained in a POM framework, $[Ru^{III}{}_2Zn_2(H_2O)_2(ZnW_9O_{34})_2]^{14-}$ (**10**), has been recently reported by Shannon and co-workers,[40] and its crystal structure is shown in Figure 5

In this structure, it is interesting to note that each Ru metal center has octahedral coordination with six oxo-bridging atoms from the POM framework, whereas the external Zn atoms contain five oxo-bridging ligands and the sixth position is occupied by an aquo ligand. It has been shown that this complex is capable of electrocatalytically oxidizing water to molecular dioxygen in a HoP at pH = 8 (phosphate buffer). This oxidation occurs at a potential close to 0.76 V vs SHE, and thus it is inferred that the oxidation takes place via a $4e^-$, $4H^+$ pathway.

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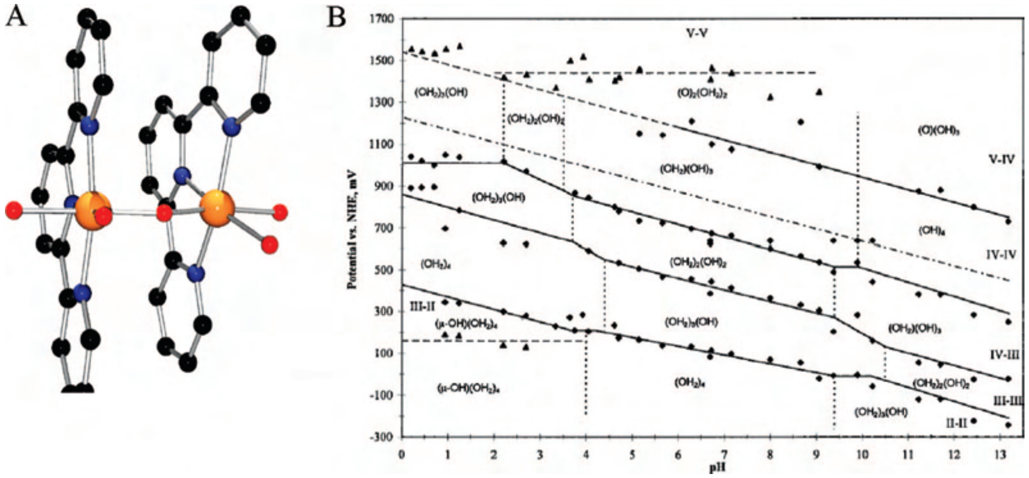

Figure 4. (A) Calculated structure and (B) Pourbaix diagram of **7**. Reprinted with permission from ref 37. Copyright 1998.

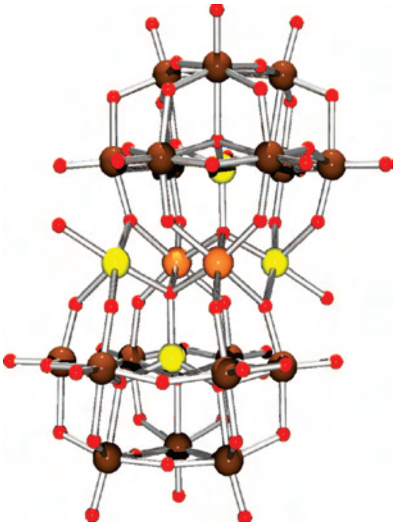

Figure 5. X-ray structure of complex **10**.[40]

For this type of complex, the presence of the Ru−O−Ru motif is critical for oxygen evolution. With the same POM scaffold but with only one Ru center, oxygen evolution is not observed, nor is it observed when the two Ru centers are replaced by Zn. Compared to the previously described water oxidation catalysts, it is interesting to see that no aquo ligands are bonded to the Ru centers and that no polypyridylic ligands are used. The presence of the $H_2O−Zn−O−Ru$ motif bears some resemblance to the $H_2O−Ca−O−Mn$ group of the OEC-PSII, where in the oxidation of water to molecular dioxygen process the electron and proton trafficking is thought to proceed by nearly opposite pathways.[12]

4. Non-Oxo-Bridging Water Oxidation Catalysts

4.1. Hbpp System. A new synthetic approach for the design of $4e^-$ water oxidation catalysts was taken by our group.[41] In order to improve the stability of the blue dimer types of complexes, the oxo-bridging group ligand was replaced by other robust and rigid bridging ligands that could not undergo the reductive cleavage deactivation pathway.[23] Furthermore, the potential cis–trans isomerization of the bis-oxo groups, as is known to happen in *cis*-$[Ru^{VI}(bpy)_2(O)_2]^{2+}$ (**11**),[38] would also be avoided. In addition, two oxo groups were placed at close proximity and with the adequate relative orientation so that an intramolecular O−O coupling could be favored. In order to meet all of these requirements, the Hbpp dinucleating bridging ligand L7 (Scheme 2) was chosen.[42] In combination with the tridentate meridional trpy ligands, the corresponding *in*,*in*-diaquo complex *in*,*in*-$[Ru_2(bpp)(trpy)_2(H_2O)_2]^{3+}$ (**12**) could be prepared, whose structure is shown in Figure 6A.

The Pourbaix diagram of this complex, as shown in Figure 6B, is radically different from that of the blue dimer mainly because of the absence of the oxo group linking the Ru metal centers. In the blue dimer, the highest oxidation state that can be reached is $Ru^{V}Ru^{V}$, which is responsible for the formation of dioxygen, whereas in **12**, the highest oxidation state that can be reached is $Ru^{IV}Ru^{IV}$. On the other hand, for **12**, both $Ru^{II}Ru^{II}$ and $Ru^{II}Ru^{III}$ oxidation states are stable, whereas for the blue dimer oxidation states lower than $Ru^{III}Ru^{III}$ cause cleavage of the oxo bridge. At pH = 1 and room temperature, complex **12** in the presence of an excess of Ce^{IV} generates molecular oxygen very fast, giving 18 metal cycles, and we have recently obtained TN numbers close to 200 under optimized system conditions.[43] Initially, Ce^{IV} is used to oxidize **12** to its $Ru^{IV}Ru^{IV}$ oxidation state, followed by a slower process involving the formation of molecular oxygen, with a pseudo-first-order rate constant of 1.4×10^{-2} s^{-1}.

$$Ru^{II}(H_2O)Ru^{II}(H_2O) + 4Ce^{IV} \rightarrow Ru^{IV}(O)Ru^{IV}(O) + 4H^+ + 4Ce^{III} \quad (5)$$

The exceptional performance of this complex is attributed to (a) a favorable disposition of the Ru=O groups that are rigidly facing each other, (b) the absence of the oxo bridge,

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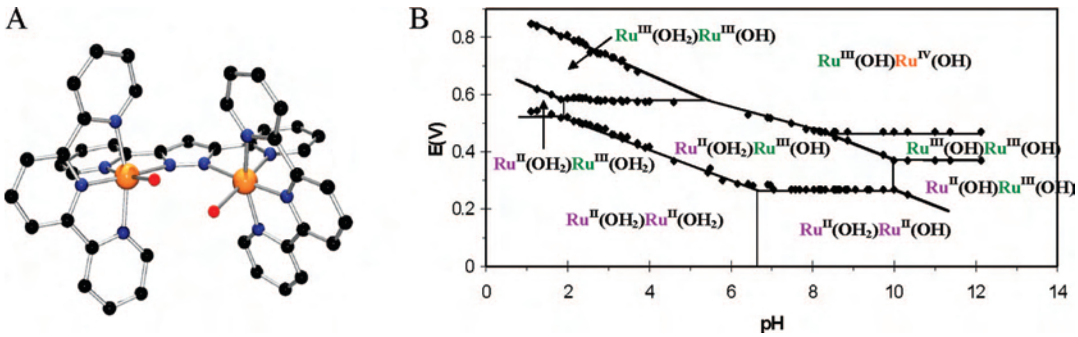


Figure 6. (A) Calculated structure and (B) Pourbaix diagram of **12**. Reprinted with permission from ref 41. Copyright 2004.

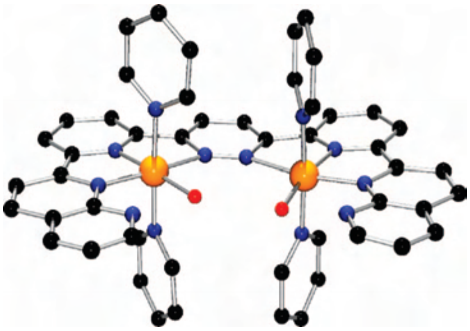


Figure 7. Calculated structure of *trans*,*trans*-[$(py)_2(H_2O)Ru^{II}(\mu$-binapypyr$)Ru^{II}(H_2O)(py)_2]^{4+}$.

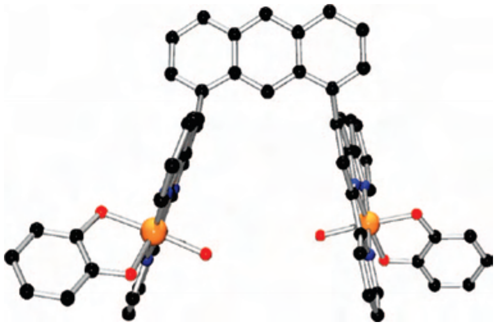
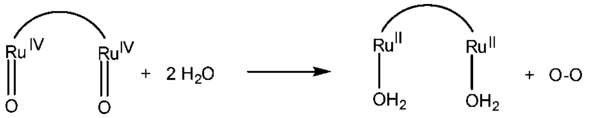


Figure 8. Calculated structure of **17** (*tert*-butyl groups from Q have been omitted). In this picture, the trpy groups of the btpyan ligand are situated perpendicular to the plane of the paper.

avoiding decomposition by reductive cleavage and by the strong thermodynamic driving force to the *trans*-dioxo formation, and (c) the competing anation side reaction that deactivates the complex in **1** taking place at a slower rate in **12** because the overall charge of the active complex, as well as the Ru oxidation states, is lower.



(6)

4.2. binapypyr System. Following a similar strategy, Thummel and co-workers prepared an octadentate (that acts as hexadentate) dinucleating neutral ligand (binapypyr, L8; Scheme 2) that contains two naphthyridyl groups coupled to a bispyridylpyridazine unit. This ligand, together with four monosubstituted pyridines, coordinates two Ru metal centers to generate the corresponding μ-Cl complex *trans*,*trans*-[(4-X-py)$_2$Ru(μ-binapypyr)(μ-Cl)Ru(4-X-py)$_2$]$^{3+}$ (X = Me, **13**; CF$_3$, **14**; NMe$_2$, **15**). The preliminary X-ray structure of **13** has been reported, and the corresponding diaquo complex is shown in Figure 7.[44] The aquo complexes have not been characterized or isolated but might likely be in equilibrium with the Cl ones when the μ-Cl complex **13** is dissolved in a 1.0 M solution of triflic acid. Furthermore, hydroxo and/or oxo species can also be formed when the initial $Ru^{II}-Cl-Ru^{II}$ complex is oxidized, as happens in related Fe complexes.[45] The addition of Ce^{IV} to this solution generates a spectacular amount of molecular oxygen, giving a TN of 538 with an efficiency of 23.6% with regard to the Ce^{IV} oxidant (the values presented here are measured via gas chromatography with a thermal conductivity detector and are much more reliable than those with the electrochemical-based method previously published).[46]

In this case, all of the ligands bonded to a corresponding aquo complex that might be derived from **13**–**15** are neutral and therefore should lead to a rather different thermodynamic scenario as compared to **1** and/or **7**. It is thus important to study the electrochemical properties of this series of complexes, in order to try to understand the potential pathways they undergo to accomplish the oxidation of water.

4.3. btpyan System. Tanaka and co-workers designed and prepared a dinucleating ligand L10, where two trpy groups are attached in an anthracene unit, as shown in Scheme 2 and Figure 8.[47] The derived dinuclear Ru complexes are also bonded to a bidentate chelating ligand, either bpy or a quinone, and finally to a monodentate ligand, that is, H_2O/OH^-, depending on the pH, $[(L)_2(H_2O)Ru(\mu$-btpyan$)Ru(H_2O)(L)_2]^{4+}$ (L = bpy, **16**; quinone, **17**), although the isolated species is the hydroxo.

Even though, unfortunately, there is no X-ray structure, modeling studies show that the btpyan ligand places the two Ru centers in close proximity, while the σ bond between the anthrancene and trpy units confers a certain degree of flexibility. These modeling studies also indicate that the two monodentate aquo ligands are juxtaposed to one another.

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Figure 9. Calculated structure of $[Ru^{III}(H\text{-}dmg)_2(imidazole)(H_2O)]^+$.

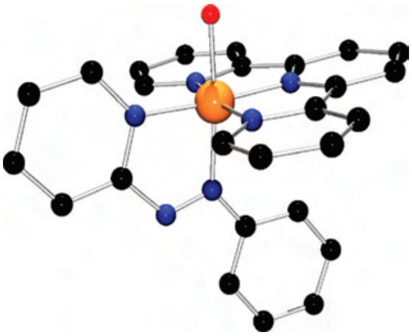

Figure 10. Calculated structure of one of the two possible isomers of **22**.

The redox properties of these complexes, which are insoluble in aqueous solution, have been characterized mainly by cyclic voltammetry in organic solvents. It is shown that, besides the metal centers, the quinone ligands are also redox-active and are capable of transferring one electron each in a chemically reversible manner.

Complex **17** has shown that it is capable of oxidizing water to molecular dioxygen in a HoP in CF_3CH_2OH with added water (10% by volume) at a rather high applied potential of 1.70 V vs Ag/AgCl, giving 21 TNs with a current efficiency of 91%. In sharp contrast, the same process where the catalyst is deposited on the surface of an ITO electrode at pH = 4 (phosphate buffer) again at a 1.70 V generates molecular oxygen with a spectacular TN of 33.500.[44b] It is not reported whether this catalyst is active or not with chemical oxidants such as Ce^{IV}.

The proposed mechanism involves the removal of $4e^-$ from the initial catalyst, $2e^-$ from the Ru centers, and $2e^-$ from the quinone ligands and the formation of a peroxo group, although there is no spectroscopic evidence for such an intermediate. The inactivity of the bpy complex **16** is in good agreement with the redox involvement of the quinone ligands in the water oxidation process. This system, despite having the largest TN values, has three serious handicaps. One is the insolubility of the complex in water such that it only works with large amounts of organic solvent. The second handicap is the high overpotential necessary for the activation of the catalyst (close to 1 V), which thermodynamically habilitates different reaction pathways. The third handicap is the lack of knowledge regarding its activity with chemical oxidants.

5. Mononuclear Complexes

Taqui-Khan et al.[48] reported four paramagnetic mononuclear complexes containing the dimethylglyoximato ligand having the general formula *trans*-$[Ru^{III}(H\text{-}dmg)_2XY]^{n+}$ (X = Y = Cl, **18**; X = Y = ClO_4, **19**; X = Cl, Y = imidazole, **20**; X = Cl, Y = methylimidazole, **21**; Figure 9), although, unfortunately, the characterization does not include X-ray crystallography. They claim that the anionic H-dmg ligands provide sufficient electron density to the metal center to lose $4e^-$ and reach oxidation state VII. They also claim that those complexes are capable of oxidizing water to molecular dioxygen by a $4e^-$ pathway, yielding 5–10 TNs. However, the nature of the process is unclear because at the potentials reported the complexes would not thermodynamically be capable of oxidizing water.

Figure 11. X-ray structure of complex **23**.[44a]

Bhattacharya et al.[49] reported a monuclear Ru−aquo complex containing trpy and 2-(phenylazo)pyridine ligands (pap, L13; Scheme 2) as a chelating ligand, $[Ru^{II}(trpy)(pap)(H_2O)]^{2+}$ (**22**; Figure 10). It is not known whether the obtained complex is either cis or trans or a mixture of both because, unfortunately, there is no thorough structural characterization either in solution or in the solid state. According to these authors, this ligand behaves as a strong π acceptor and thus produces a strong enhancement of the III/II redox potentials in the case of the corresponding Ru−Cl complex. Complex **22** has been reported to oxidize water to molecular dioxygen using Ce^{IV} as an oxidant, although again, as in the previous case, the redox potentials reported are too low to be able to perform this reaction. The formed oxygen is detected electrochemically but has not been quantified.

Thummel et al.[44] have reported three mononuclear $Ru-OH_2$ complexes with the new meridional ligand 2,6-bis(2′-naphthyridyl)-4-*tert*-butylpyridine (binapy, L14; Scheme 2) of the general formula *trans*-$[Ru(binapy)(4\text{-}X\text{-}py)_2(H_2O)]^{2+}$ (X = Me, **23**; CF_3, **24**; NMe_2, **25**; Figure 11). Given the types of ligands bonded to the metal center and the two-electron-transfer nature associated with a single

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Table 1. Comparative Catalyst Performance

catalyst	conditions	oxidant	ox./cat.	TN[a]	eff[b]	k_{o2}[c] (s^{-1})	technique[d]	ref
1	0.1 M $HClO_4$	Ce^{IV}	88	13.2	60	4.2×10^{-3}	GC	26, 31
1/Nafion	0.1 M $HClO_4$	Ce^{IV}	3100	3.1	0.4	2.4×10^{-3}	GC	31
3[e]	0.1 M H_3PO_4	$E_{app} = 1.39$ V		4.7	90.0		GC	33
4 and **5**	0.1 M CF_3SO_3H	Ce^{IV}	50	2.7	21.6	7.4×10^{-9}[f]	GC	34
6	1.0 M CF_3SO_3H	Co^{III}					GC	35
7	pH = 6[g]	$E_{app} > E°'(VI,V)$[h]		3.0			GPOE	37, 39
12	0.1 M CF_3SO_3H	Ce^{IV}	102	18.6	73.0	1.4×10^{-2}		41
			1000	173	69.2		GC[i]	43
13	1.0 M CF_3SO_3H	Ce^{IV}	9120	538	23.6		GC[j]	44a, 46
17/ITO	pH = 4[k]	$E_{app} = 1.70$ V[l]		500 (6730)[m]	95		GC	47
				2400 (33 500)	95			
20	1.0 M $HClO_4$	Ce^{IV}	200	7.4	14.8		volumetric	48
23	1.0 M CF_3SO_3H	Ce^{IV}	9120	580	25		GPOE	44a, 46

[a] Moles of oxygen generated per mole of Ru catalyst. [b] For chemical oxidations, the efficiency is calculated with regard to the oxidant used, assuming that 1 mol of O_2 needs 4 mol of Ce^{IV}; for electrochemical oxidations, the efficiency is reported as the current efficiency. [c] k_{o2} defined as the intrinsic activities of the catalyst under a large excess of Ce^{IV} (ox./cat. ratios between 100/1 and 300/1; see ref 31). [d] Oxygen measurement technique; GC, gas chromatography; GPOE, gas-phase oxygen electrode. [e] The results are described for complex **3**, which contains the bridging bis-bpy ligand L2c. [f] Initial rate constant. [g] Terephthalic acid/monoterephthalate anion buffer. [h] Redox potential applied past the redox potential of the $Ru^{VI}-O-Ru^{V}/Ru^{V}-O-Ru^{V}$ wave. [i] Reference 43. [j] Thummel, R. A. Personal communication. [k] Phosphate buffer. [l] Redox potentials vs Ag/AgCl. It represents an overpotential of 0.99 V with regard to thermodynamic oxidation of water to molecular dioxygen via the $4e^-$, $4H^+$ pathway. [m] In parentheses are values obtained after reutilization upon regeneration of the initial pH. The values in the first row are those reported in ref 47a, whereas those in the second row are those reported in ref 47b.

Ru−OH_2 group, the redox potentials of **23**–**25** should not strongly differ from those of $Ru(trpy(bpy)(H_2O)]^{2+}$ (**26**),[50] and the reactivity should be similar. Thus, one would not expect these systems to oxidize water to dioxygen. However, not only has it been recently reported that they can oxidize water but also their performance is impressive, with TNs in the range of 50–580. The Ru−OH_2 complexes derived from **23**–**25** constitute a family of highly interesting complexes whose redox properties and reactivities should be thoroughly investigated.

Finally, a dinuclear Ru complex generated in situ, from a mononuclear one, *trans*-$[Ru^{III}(Hedta)(H_2O)]$ (**26**), was initially reported by Baar and Anson[51] to oxidize water to molecular dioxygen. However, Hurst et al. carefully repeated the experiments and reported[52] that the complex did not generate any oxygen at all but instead produced copious amounts of CO_2.

6. Conclusions and Future Prospects

Table 1 presents a comparative summary of selected Ru complexes that are capable of oxidizing water to molecular dioxygen. It is clear from the table that, so far, dinuclear Ru complexes are the best, although the performance of the mononuclear catalysts should not be ignored. One of the key features of any dinuclear complex is the bridging ligand between the two metal centers because it determines the degree of electronic coupling[53] between the two metals. Furthermore, the bridging ligand also has strong consequences with regard to the geometry of the complex, and this geometry is especially important in determining the relative disposition of the active ligands in the catalytic process.

The bridging ligands used with the more effective catalysts are the dianionic O^{2-} for the blue dimer **1**, the monoanionic pyrazolate moiety for the deprotonated Hbpp ligand in **12**, and the neutral pyridazine group for the Thummel complex **13**. Those ligands not only have different Coulombic charges and thus different donation capabilities but also produce a radically different electronic coupling between the metal centers. Furthermore, whereas the oxo bridge will generate a relatively flexible scenario, the other two ligands are rigid. Thus, from the performance of these complexes, it can be deduced that a wide range of ligand architectures and electronics can be used to design water oxidation catalysts. Assuming that complexes **1**, **12**, and **13** generate oxygen via dioxo formation, it is interesting to realize that the corresponding $(Ru{=}O)_2$ complex will have Coulombic charges of 4+, 3+, and 4+, respectively. This is also an important factor because for both **1** and **12** anation has been reported to be a side reaction that deactivates the catalyst. Thus, the important target in this field is an anion that does not coordinate to the metal centers, is not oxidized by the catalyst, and does not negatively interfere with the catalytic cycle or a system that could work near neutral pH, where the salt concentration can be substantially reduced.

For the trpy dimer **7**, the catalytic performance with regard to water oxidation is poor both in the HoP and in the HeP. The main problem of this catalyst is associated with the strong tendency to isomerize from the original *cis*-dioxo disposition to the *trans*-dioxo, arresting the catalytic cycle before it can carry out the oxidation of water. Thus, for future catalyst design, it seems important that the two active oxo groups be situated on different metal centers. On the other hand, the Shannon POM, **10**, is interesting in the sense that the ligands coordinated to the Ru centers are all oxo bridges with no polypyridylic ligands. This system is conceptually different from all of the dinuclear complexes previously described and opens up new avenues for designing active water oxidation catalysts.

Another interesting approach comes from the presence of auxiliary ligands active in the catalytic cycle. Thus, in Tanaka's dinuclear Ru complex **17**, it is proposed that each

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(53) Balzani, V.; Juris, A.; Venturi, M. *Chem. Rev.* **1996**, *96*, 759.

metal center accepts an electron and each quinone also accepts one electron, generating the corresponding semiquinone, with an overall 4e$^-$ transfer.

The mononuclear complexes capable of oxidizing water to molecular dioxygen also constitute an interesting group of catalysts that deserve to be carefully studied because the pathways through which they function are not well understood. For the case of the mononuclear complexes containing monodentate ligands such as those of Taqui-Khan et al., **18–21**, a potential pathway *may* involve the decoordination of one of the monodentate ligands upon oxidation of the original complex, leading to the corresponding oxo-bridged dimers. For instance, *trans*-[Ru^{III}(H-dmg)$_2$(Cl)(imidazole)] (**20**) may lose an imidazole ligand to generate the corresponding oxo dimer, *trans*,*trans*-[(H-dmg)$_2$(H$_2$O)Ru^{III}(μ-O)Ru^{III}(H$_2$O)(H-dmg)$_2$)]$^{2+}$ (**27**), whose structure has been calculated at the ZINDO level and is depicted in Figure 12. Although this pathway is pure speculation, the process is not uncommon because, for instance, the blue dimer is prepared by oxidation of Ru^{II}(bpy)$_2$Cl$_2$.[24] This complex **27** might have the adequate redox potentials and proton composition to undergo a 4H$^+$, 4e$^-$ transfer and generate molecular oxygen in a catalytic manner.

The variety of complexes that are capable of oxidizing water to molecular dioxygen, using quite different ligands, together with the basic knowledge needed for this reaction to proceed catalytically, coupled to the urgent need of our society for efficient water oxidation catalysts, will most likely foster the development of new catalysts in the near future. For this development, it is important to advance our mechanistic understanding of these processes to properly design improved catalysts that use water and sunlight as the clean and environmentally respectful fuel of the future.

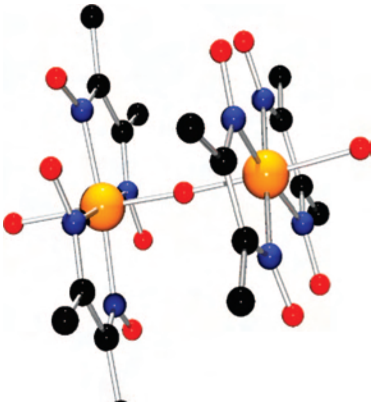

Figure 12. Calculated structure of **27**.

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