Binuclear [(cod)(Cl)Ir(bpi)Ir(cod)]⁺ for Catalytic Water Oxidation

*Wojciech I. Dzik,^a Sara E. Calvo,^a Joost N. H. Reek,^a Martin Lutz,^b Miguel A. Ciriano,^c Cristina Tejel,^c
Dennis G. H. Hetterscheid,^a and Bas de Bruin^{*a}*

^a Van 't Hoff Institute for Molecular Sciences, University of Amsterdam, Science Park 904, 1098 XH
Amsterdam (the Netherlands), Fax: (+31) 20 5255604. E-mail: b.debruin@uva.nl

^b Bijvoet Center for Biomolecular Research, Utrecht (The Netherlands)

^c Instituto de Ciencia de Materiales de Aragón (ICMA), CSIC-Universidad de Zaragoza (Spain)

Abstract: The binuclear iridium complex [(cod)(Cl)Ir(bpi)Ir(cod)]PF₆ (bpi = pyridine-2-ylmethylpyridine-2-ylmethylethylamine; cod = 1,5-cyclooctadiene) reveals a noteworthy asymmetric binuclear coordination geometry, wherein the bpi ligand acts as a heteroditopic ligand and shows an unusual π -coordinated imine moiety. This species is an effective precatalyst for water oxidation. After a short incubation time the catalyst reveals a turnover frequency of 3400 mol mol⁻¹ s⁻¹ with overall turnover number >1000.

Our current global energy consumption is primarily based on combustion of fossil fuels,¹ but it is questionable how long we can proceed in this way. Fossil fuel supplies are limited, while global demands are rapidly increasing. Moreover, political issues, pollution and climate change put heavy demands on our energy consumption habits. Long-term alternatives will largely depend on one of our environmentally friendly and abundant energy source: sunlight. Storage of energy, directly or indirectly produced by sunlight, in the form of chemical energy (e.g. hydrogen) to produce renewable fuels for our cars and airplanes is one of the most challenging problems that scientists need to solve within the next decades. One sensible way to do this is to use water as a resource, since water is the most abundant, cheap and sustainable source of electrons on our planet.

The water oxidation half-reaction $\text{O}_2(\text{g}) + 4\text{H}^+(\text{aq}) + 4\text{e}^- \rightarrow 2\text{H}_2\text{O}$ has a thermodynamic redox potential $E^0 = +1.23 - (0.059 \cdot \text{pH}) \text{ V}$. This process is however deceptively simple, because important kinetic limitations of oxidation of water are usually encountered. As a rule of thumb, non-catalyzed processes oxidation of H_2O to O_2 occurring at observable rates generally require an overpotential of $\sim 0.6 \text{ V}$ (this holds both for electrochemical and chemical oxidation of water). Hence, it is important to search for new, efficient and fast water oxidation catalysts to lower this barrier.² Only a few synthetic water oxidation catalysts are known to date,^{3,4} and none of them approach the turnover frequencies, turnover numbers and mild over potentials that are required to efficiently use water as a source of electrons in large scale fuel synthesis.⁵ Several bio-inspired Mn-based structural and functional model systems of the natural oxygen evolving complex (OEC) in green plants have been developed in an attempt to achieve artificial water oxidation catalysis.⁶ However, only a few of these are actually capable of converting water into dioxygen,⁵ and all of these are quite slow or too unstable to be of any practical use.⁶ Besides manganese, also ruthenium bipyridine complexes have received much attention since the mid 1980's, when the first functional Ru-based water oxidation catalyst was reported by Meyer, *i.e.* the 'blue dimer'.⁶ Many (mononuclear, binuclear and multinuclear) variations of the original design have been synthesized since.^{7,8}

Remarkably, poorly defined, heterogeneous water oxidation catalysts tend to outperform their well-defined homogeneous counterparts, and significant results were recently reported using iridium colloids,^[9] a cobalt phosphate system,¹⁰ and recently even a molecular iron complex.¹¹ The two latter reports are of particular interest, as they comprise rather low cost systems based on inexpensive cobalt and iron. However, the most stable and durable and amongst the fastest catalysts reported to date are based on iridium, comprising colloidal Ir systems,¹² as well as a series of well-defined mononuclear Ir molecular complexes (see Figure 1) as developed by the groups of Bernhardt¹³ and Crabtree.¹⁴

Figure 1. Fast and robust iridium water oxidation catalysts and some representative non-iridium catalysts. See also Table 1.

In analogy with the binuclear Ru compounds developed by Meyer, we argued that binuclear Ir compounds could perhaps outperform the mononuclear analogs in the overall $4e^-$ oxidation process of water. Hence we set out to utilize N-donor ligands to prepare binuclear Ir compounds and utilize these in water oxidation catalysis.

Building on our experience with (doubly) deprotonated bpa ligands ($\text{bpa} = \text{Py}-\text{CH}_2-\text{NH}-\text{CH}_2\text{Py}$) in the preparation of low-valent binuclear group 9 TM complexes,¹⁵ we argued that similar binuclear Ir species in a higher oxidation state might be accessible by using the imine analog bpi ($\text{bpi} = \text{Py}-\text{CH}=\text{N}-\text{CH}_2\text{Py}$).

Scheme 1. Synthesis of complex **[1]**PF₆.

Indeed, reaction of bpi with $[\{\text{Ir}(\mu\text{-Cl})(\text{cod})\}_2]$ in MeOH followed by precipitation with KPF₆ produced the cationic binuclear compound $[(\text{cod})(\text{Cl})\text{Ir}(\text{bpi})\text{Ir}(\text{cod})]\text{PF}_6$ (**[1]**PF₆). NMR and mass spectra reveal the binuclear nature of the complex, which was obtained in 61% isolated yield. Single crystals suitable for X-ray diffraction were obtained from CH₃CN/Et₂O (1:5). The molecular structure of cation **1**⁺ is shown in Figure 2.

Figure 2. Structure (ORTEP at 50% level) of cation **1**⁺. Hydrogen atoms, the PF₆[−] counter ion and non-coordinated acetonitrile molecules are omitted for clarity.

The structure reveals a noteworthy and rather unusual π -coordination mode of the bpi imine moiety. To our best knowledge this appears to be the first example of a π -bound imine moiety for iridium. Sigma-coordination of the imine nitrogen to the first iridium atom (Ir2) appears to activate the imine for η^2 -coordination to the other iridium (Ir1). The bpi ligand in $\mathbf{1}^+$ acts as a heteroditopic dicompartmental ligand, with two distinct compartments hosting a Ir(cod) fragment in one compartment and an Ir(Cl)(cod) fragment in the other. The first compartment functions as a heterobidentate *N,N'*-ligand fragment consisting of one of the Py donors and the imine nitrogen, thus hosting a square-planar Ir(cod) fragment (Ir2). The imine π -orbitals and the other Py-donor remain available to host the Ir(Cl)(cod) fragment. The coordination geometry around Ir1 is best described as a trigonal bipyramid, with pyridine N1 and one of the olefinic double bonds of cod (C31–C32) at the axial positions. The chloro ligand Cl, the other cod double bond (C35–C36) and the imine double bond (C26–N3) span the trigonal plane and both are coplanar to the equatorial plane. This particular disposition is appropriate for optimal π -back donation from the metal to both double bonds.

As a result of increased metal-to-ligand π -back donation in the trigonal plane of Ir1, the cod double bond C35-C36 of 1.414(3) Å is somewhat elongated compared to the axially coordinated cod double bond C31-C32 of 1.389(3) Å. This effect is however relatively small (see Table S1 in the Supporting Information). The imine π -coordination is associated with much stronger π -back donation, presumably due to nitrogen σ -coordination of this same imine to the other iridium atom making this fragment a strong π -acceptor ligand. The imine C26–N3 bond in $\mathbf{1}^+$ (1.407(3) Å) is substantially elongated as compared to imine C–N bonds of Ir complexes in which the imine only adopts the typical σ -coordination mode ($\sim$ 1.30 Å).¹⁶ As a result the irida(III)-aza-cyclopropane description contributes substantially to the electronic structure of this compound (Scheme 2).

Scheme 2. Relevant resonance contributions to $\mathbf{1}^+$.

Water oxidation activity

Complex $[\mathbf{1}]\text{PF}_6$ proves to be an excellent precatalyst for water oxidation catalysis, generating a fast and robust active catalyst upon treatment with cerium ammonium nitrate (Ce^{IV}). Full conversion of 550 mg $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$ in 5 mL of water in the presence of 0.05 mol % of $[\mathbf{1}]\text{PF}_6$ led to quantitative formation of O_2 gas (5.5 mL) within 50 minutes.

Kinetic studies reveal that the reaction is first order in both the Ce^{IV} oxidant and in the iridium precatalyst $[\mathbf{1}]\text{PF}_6$ (Figure 3). At very low iridium concentrations ($< 8 \times 10^{-5}$ M), the reaction profile shows an incubation time, which becomes shorter at higher iridium concentration ($> 1.2 \times 10^{-4}$ M). This suggests that the actual active catalyst is formed from the precatalyst in an intermolecular reaction. The kinetic experiments show a clear first order behavior in both cerium and the precatalyst $\mathbf{1}^+$, indicating that a well-defined active species is formed from the precatalyst.

Figure 3. First order rate behaviour of water oxidation vs the concentration of $[\mathbf{1}]\text{PF}_6$.

The well-behaved kinetic data are inconsistent with catalysis by heterogeneous iridium oxide particles.¹⁷ The most likely explanation for the obtained kinetic data is the formation of a soluble molecular compound or cluster as the active water oxidizing catalyst.

Fitting the graph in Figure 3 to the overall rate equation of the reaction ($\text{rate} = k_{\text{obs}}[\text{Ce}^{\text{IV}}] = k[\text{Ir}][\text{Ce}^{\text{IV}}]$) yields the second order rate constant $k = 4.7 \text{ M}^{-1} \text{ s}^{-1}$. This value translates to a turnover frequency (TOF) of $3400 \text{ mol mol}^{-1} \text{ h}^{-1}$ (O_2 per mol precatalyst) under the conditions applied. The active species that is formed after incubation is among the fastest reported molecular water oxidation catalysts (see Table 1). Polyoxometalate cobalt clusters show much higher initial turnover frequencies, but the total turnover number is limited to roughly 60.¹⁸ In case of $[\mathbf{1}]\text{PF}_6$ no significant catalyst deactivation was observed after 2 hours and at least 1000 turnovers. In terms of rate and robustness the catalyst formed from $[\mathbf{1}]\text{PF}_6$ displays a similar performance as the system reported by Crabtree.¹⁴

Table 1. Comparison of water oxidation rate of our new catalysts with those reported in literature.

Catalyst	TOF ($\text{mol mol}^{-1} \text{ h}^{-1}$)	TON (mol mol^{-1})	Ref.
$[\mathbf{1}]\text{PF}_6$	3400 ^(a)	> 1000 ^(b)	This paper
A	20	2500	13
B	3000	1500	14
C	80	220	14
D	850	550	8b
E	4700	16	11
$[\text{Co}_4(\text{H}_2\text{O})_2(\text{PW}_9\text{O}_{34})_2]^{10-}$	18000	60	10

(a) TOF = $1700 \text{ mol mol}^{-1} \text{ h}^{-1}$ (mol O_2 per mol iridium)

(b) Lower limit based on quantitative Ce^{IV} consumption.

At this point we can only speculate on the mechanism and the exact nature of the active species formed. It is tempting to ascribe the activity to the bimetallic nature of the catalyst precursor, forming a bis-iridium active catalyst under the reaction conditions applied. The rich redox chemistry of iridium,

allowing several oxidation states including a relatively easily accessible Ir^V is likely also an important factor.

In conclusion, we synthesized the new cationic binuclear iridium compound [(cod)(Cl)Ir(bpi)Ir(cod)]PF₆, **[1]**PF₆, which reveals a noteworthy and unusual π -coordination mode of the bpi-imine moiety. This gives rise to an unusual coordination geometry and an oxidation state ambiguity for one of the two iridium atoms. The species is an excellent precatalyst for water oxidation catalysis using Ce^{IV} as the oxidant. Further studies regarding the robustness, scope, nature of the active species, and the mechanism of water oxidation by **1**⁺ are in progress.

Acknowledgements

Financial support from the European Research Council (ERC Grant Agreement 202886-CatCIR), NWO-CW (VIDI grant 700.55.426, VENI grant 700.59.410), the MEC/FEDER (Project CTQ2008-03860, Spain), and the University of Amsterdam is gratefully acknowledged.

Supporting Information Available.

Crystallographic information (cif-file) containing data for complex **[1]**PF₆, synthetic procedure, kinetic plots of the water oxidation reactions, and selected NMR spectra. This material is available free of charge via the Internet at <http://pubs.acs.org>.

¹ Lewis, N. S.; Nocera, D. G. *Proc. Natl. Acad. Sci. USA* **2006**, *103*, 15729.

² Dau, H.; Limberg, C.; Reier, T.; Risch, M.; Roggan, S.; Strasser, P. *ChemCatChem* **2010**, *2*, 724.

³ a) Yano, J.; Kern, J.; Sauer, K.; Latimer, M. J.; Pushkar, Y.; Biesiadka, J.; Loll, B.; Saenger, W.; Messenger, J.; Zouni, A.; Yachandra, V. K. *Science* **2006**, *314*, 821; b) Meyer, T. J.; Huynh, M. H. V.; Thorp, H. H. *Angew. Chem. Int. Ed.* **2007**, *46*, 5284; c) Dasgupta, J.; Ananyev, G. M.; Dismukes, G. C. *Coord. Chem. Rev.* **2008**, *252*, 347; d) Barber, J. *Chem. Soc. Rev.* **2009**, *38*, 185.

⁴ Cady, C. W.; Crabtree, R. H.; Brudvig, G. W. *Coord. Chem. Rev.* **2008**, *252*, 444.

-
- ⁵ Storing the equivalent of today's energy consumption would require splitting 10^{15} moles of water per year. This is about 100 times the scale of the Haber Bosch reaction. The TON required depends on the abundance of the catalyst. See ref 10.
- ⁶ Mullins, C. S.; Pecoraro, V. L. *Coord. Chem. Rev.* **2008**, *252*, 416.
- ⁷ Sala, X.; Romero, I.; Rodríguez, M.; Escriche, L.; Llobet, A. *Angew. Chem. Int. Ed.* **2009**, *48*, 2842.
- ⁸ a) Duan, L.; Fischer, A.; Xu, Y.; Sun, L. *J. Am. Chem. Soc.* **2009**, *131*, 10397. b) Duan, L.; Xu, Y.; Gorlov, M.; Tong, L.; Andersson, S.; Sun, L. *Chem. Eur. J.* **2010**, *16*, 4659.
- ⁹ a) Hara, M.; Mallouk, T. E. *Chem. Commun.* **2000**, 1903; b) Han, H.; Frei, H.; *J. Phys. Chem. C* **2008**, *112*, 16156.
- ¹⁰ Kanan, M. W.; Nocera, D. G. *Science* **2008**, *321*, 1072.
- ¹¹ Ellis, W. C.; McDaniel, N. D.; Bernhard, S.; Collins, T. J. *J. Am. Chem. Soc.* **2010**, *132*, 10990.
- ¹² Morris, N. D.; Suzuki, M.; Mallouk, T. E. *J. Phys. Chem. A* **2004**, *108*, 9115.
- ¹³ McDaniel, N. D.; Coughlin, F. J.; Tinker, L. L.; Bernhard, S. *J. Am. Chem. Soc.* **2008**, *130*, 210.
- ¹⁴ Hull, J. F.; Balcells, D.; Blakemore, J. D.; Incarvito, C. D.; Eisentein, O.; Brudvig, G. W.; Crabtree, R. H. *J. Am. Chem. Soc.* **2009**, *131*, 8730.
- ¹⁵ a) Tejel, C.; Del Rio, M. P.; Ciriano, M. A.; Reijerse, E. J.; Hartl, F.; Zális, S.; Hetterscheid, D. G. H.; Tschlis i Spithas, N.; de Bruin, B. *Chem. Eur. J.* **2009**, *15*, 11878. b) Tejel, C.; Ciriano, M. A.; Del Rio, M. P.; Hetterscheid, D. G. H.; Tschlis i Spithas, N.; Smits, J. M. M.; de Bruin, B. *Chem. Eur. J.* **2008**, *14*, 10932. c) Tejel, C.; Ciriano, M. A.; Del Rio, M. P.; Van den Bruele, F. J.; Hetterscheid, D. G. H.; Tschlis i Spithas, N.; de Bruin, B. *J. Am. Chem. Soc.* **2008**, *130*, 5844.
- ¹⁶ For example, the pyridine-2-imine complex [Ir(cod)(ppeI)I] has an imine C–N bond distance of 1.30(2) Å: Zassinovich, G.; Bettella, R.; Mestroni, G.; Bresciani-Pahor, N.; Geremia, S.; Randaccio, L.; *J. Organomet. Chem.*, **1989**, *370*, 187.

-
- ¹⁷ Unless these would be formed in a highly controlled fashion leading to defined colloidal (nano)particles with an uniform size and surface area. This seems however highly unlikely under the applied reaction conditions.
- ¹⁸ Yin, Q.; Tan, J. M.; Besson, C.; Geletii, Y. V.; Musaev, D. G.; Kuznetsov, A. E.; Luo, Z.; Hardcastle, K. I.; Hill, C. L. *Science* **2010**, 328, 342.