The Use of a Vanadium Species As a Catalyst in Photoinduced Water Oxidation

Marie-Pierre Santoni,*[†] Giuseppina La Ganga,[†] Viviana Mollica Nardo,[†] Mirco Natali,[‡] Fausto Puntoriero,[†] Franco Scandola,*[‡] and Sebastiano Campagna*[†,§]

[†]Dipartimento di Scienze Chimiche, Università di Messina, and Centro Interuniversitario per la Conversione Chimica dell'Energia Solare (SOLAR-CHEM), sezione di Messina, 98166 Messina, Italy

[‡]Dipartimento di Scienze Chimiche e Farmaceutiche, Università di Ferrara, and Centro Interuniversitario per la Conversione Chimica dell'Energia Solare (SOLAR-CHEM), sezione di Ferrara, 44121 Ferrara, Italy

[§]ISOF-CNR, 40129 Bologna, Italy

Ⓢ *Supporting Information*

ABSTRACT: The first water oxidation catalyst containing only vanadium atoms as metal centers is reported. The compound is the mixed-valence $[(V^{IV}_5V^V_1)O_7(OCH_3)_{12}]^-$ species, **1**. Photoinduced water oxidation catalyzed by **1**, in the presence of $Ru(bpy)_3^{2+}$ (bpy = 2,2′-bipyridine) and $Na_2S_2O_8$, in acetonitrile/aqueous phosphate buffer takes place with a quantum yield of 0.20. A hole scavenging reaction between the photochemically generated $Ru(bpy)_3^{3+}$ and **1** occurs with a bimolecular rate constant of 2.5×10^8 M^{-1} s^{-1}. The time-resolved formation of the oxidized molecular catalyst $\mathbf{1}^+$ in bimolecular reactions is also evidenced for the first time by transient absorption spectroscopy. This result opens the way to the use of less expensive vanadium clusters as water oxidation catalysts in artificial photosynthesis schemes.

Artificial photosynthesis, that is the conversion of light energy into chemical energy, is currently attracting much interest, for both fundamental and applicative reasons.[1−5] The achievement of an efficient artificial photosynthesis, aimed to produce high-energy content chemical species from low-energy content chemical species using solar energy as the energy source, would be a sort of Holy Grail of modern science,[2] as it could solve the problems connected with the intermittency and low-density of solar energy.[4,5] Moreover, solar energy is diffuse all over the world, and the social and political problems somehow connected with localization of fossil energy sources would be largely alleviated.[4]

Any scheme of artificial photosynthesis includes water oxidation as a crucial step.[6] As a consequence, in the past few years much work has been devoted to identify new good catalysts for water oxidation and integrate them into photosynthetic schemes. Among molecular catalysts, whereas probably the most efficient water oxidation molecular catalysts are ruthenium compounds,[7−10] catalysts based on earth-abundant metals are particularly attractive. Water oxidation catalysts containing only earth-abundant metals such as cobalt,[11] manganese,[12] iron,[13] copper,[14] and molybdenum[15] have been studied. Surprisingly, in spite of the rich redox chemistry displayed by vanadium compounds,[16] no vanadium species has been reported to behave as a molecular water oxidation catalyst yet.

Here we report on the photoinduced water oxidation obtained by using a sacrificial system made of $Ru(bpy)_3^{2+}$ (bpy = 2,2′-bipyridine) as a photosensitizer, $Na_2S_2O_8$ as the sacrificial acceptor, and a methoxo-polyoxovanadium cluster, namely $(N-Bu_4)[V_6O_7(OCH_3)_{12}]$ (**1**; $Bu = n-C_4H_9$),[17] as the water oxidation catalyst. It is the first time, to the best of our knowledge, that a vanadium species is demonstrated to play the role of a water oxidation catalyst, and this result introduces the large and tunable class of polyoxovanadate species into the field, paving the way for further exploration. Moreover, whereas in most of the formerly studied polyoxometalated water oxidation catalysts the polyoxometalated unit(s) were mainly used as stabilizing units, with the catalytically active metals not belonging to the polyoxometalated scaffold,[9,11d,h] in the present case the catalytically active center is the polyoxometalated framework.

Compound **1** (see Figure 1) has been previously reported by Daniel and Hartl;[17] it is a cluster formally derived from the highly symmetrical Lindqvist structure $[M_9O_{19}]^{n−}$,[18] where the 12 μ-bridged oxo ligands are substituted by methoxo ligands. Alkoxo-polyoxovanadium clusters similar to **1** exhibit a quite rich redox activity, with a series of thermodynamically stable redox isomers of general formula $[V^{IV}_nV^V_{6−n}O_7(OR)_{12}]^{(4−n)}$ (R = alkyl groups), of which several species have been synthesized and characterized.[17] In particular, compound **1** exhibits six one-electron redox processes in acetonitrile (although not all of them are reversible), in the potential window $−1.0 \div +2.2$ V vs ferrocene/ferrocinium couple.[17b] The whole range of electrochemical transformation is included, from full reduction to the isovalent vanadium(IV) cluster $[V^{IV}_6O_7(OCH_3)_{12}]^{2−}$ to complete oxidation to the isovalent vanadium(V) cluster $[V^V_6O_7(OCH_3)_{12}]^{4+}$.[17b] The absorption spectrum of each redox isomer has also been identified,[17b] evidencing the presence of intervalence bands, which allowed classification of the mixed-valence isomers as class II species, according to the Robin and Day formalism.[19] The redox isomer we prepared,
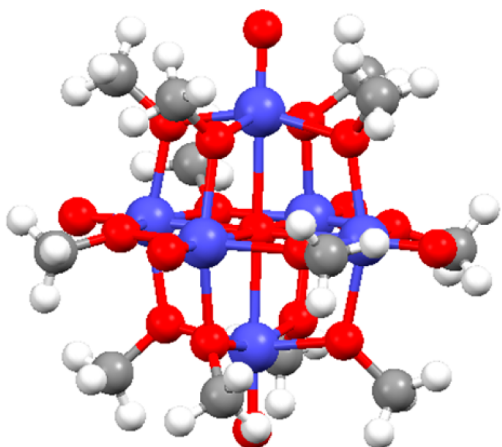
Figure 1. Ball-and-stick representation of $[(V^{IV}_5V^V_1)O_7(OCH_3)_{12}]^-$ (**1**; counterion omitted for clarity; C = gray; H = white; O = red; V = blue).

following literature procedure,[17] is the $[(V^{IV}_5V^V_1)O_7(OCH_3)_{12}]^-$ species.

The cyclic voltammogram (CV) of **1** in 1:1 (v/v) acetonitrile/40 mM aqueous phosphate buffer (pH 7) is shown in Figure 2: two reversible oxidation processes, similar to
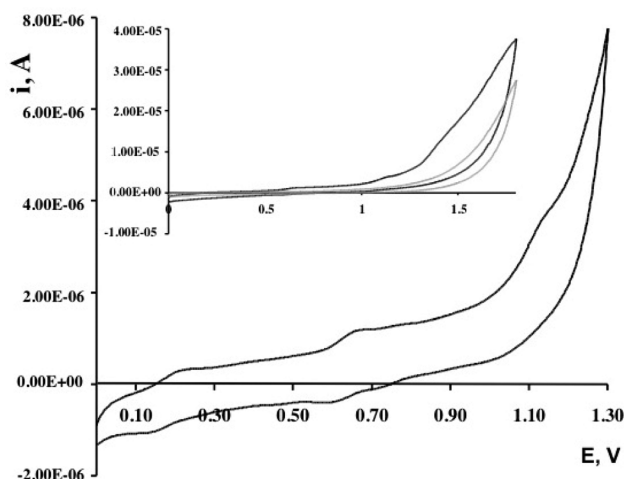

Figure 2. Cyclic voltammogram of **1** (1×10^{-3} M) in acetonitrile/40 mM aqueous phosphate buffer (pH 7). Volts are vs SCE. Scan rate: 20 mV s^{-1}. In the inset, the potential window has been extended to better visualize the water discharge.

those reported in acetonitrile (see Supporting Information, Figure S1),[17b] occur in the potential window $0.0 \div +1.0$ V vs SCE. The first process takes place at about 0.20 V and the second one at about 0.65 V; they are attributed to successive one-electron oxidation processes, leading to the $[(V^{IV}_3V^V_3)O_7(OCH_3)_{12}]^+$ species. At about 1.10 V, another oxidative process seems to take place. This process is partially overlapped with a catalytic wave, starting at about 1.20 V, which can be attributed to water discharge, so it cannot be clearly defined.

After recording of the cyclic voltammogram which was performed up to +1.70 V, the working electrode used was checked and no traces of any deposited material was found.[20] The electrode was then immersed into the solvent mixture, and no water oxidation discharge was recorded. This would exclude the formation of heterogeneous water oxidation catalysts on the

electrode surface upon oxidation of **1**.[20] At this stage, any mechanistic conclusion would be premature; the CV in Figure 2, which indicates that several successive one-electron oxidation processes involving different metal centers precede the catalytic wave, could suggest that the catalytic pathway involves multiple sites, but it does not exclude a single-site process, in particular in the case of peroxidic intermediates.

Photoinduced water oxidation was investigated by using a sacrificial system made of Ru(bpy)$_3^{2+}$ (2×10^{-4} M), **1** (6×10^{-5} M), and Na$_2$S$_2$O$_8$ (10 mM) in 2 mL of acetonitrile/phosphate buffer, and excitation at $\lambda = 450$ nm: Figure 3 shows
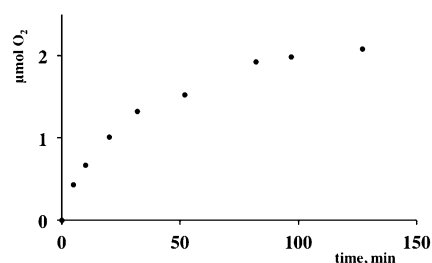

Figure 3. Oxygen production upon photoinduced water oxidation from a Ru(bpy)$_3^{2+}$ (2×10^{-4} M)/**1** (6×10^{-5} M)/Na$_2$S$_2$O$_8$ (10 mM) system in acetonitrile/phosphate buffer; excitation wavelength, 450 nm (see text). System stops producing oxygen likely as a consequence of degradation of sensitizer, as usually found in similar systems.[23]

the time dependence of O$_2$ production so obtained, measured using a method previously described.[21] The photochemical quantum yield, Φ, for molecular oxygen production, at $\lambda_{exc} = 450$ nm, was 0.20, indicating that 40% of photons absorbed by the photosensitizer Ru(bpy)$_3^{2+}$ are efficiently used to produce O$_2$, assuming the generally accepted reaction scheme in which the sacrificial persulfate electron acceptor is the primary quencher (by irreversible electron transfer) of the metal-to-ligand charge-transfer (MLCT) excited state of Ru(bpy)$_3^{2+}$, with production of the oxidized sensitizer Ru(bpy)$_3^{3+}$, which successively undergoes a hole scavenging process with **1**; the sequence of the above-mentioned individual steps is to be repeated several times, until the catalytically active state of **1** is reached.[22,23] This Φ value is quite promising when compared to that obtained for the photochemical quantum yield of O$_2$ production using the cobalt(III) cubane-type species $[Co^{III}_4(\mu\text{-}O)_4(\mu\text{-}CH_3COO)_4(NC_5H_5)_4]$, that is 0.13, under almost identical experimental conditions (the main difference was the presence of borate buffer, at pH 8, instead of the phosphate buffer, at pH 7, here used).[11e,24]

An important parameter to determine the efficiency of a molecular catalyst in photoinduced water oxidation is the rate constant of hole scavenging, that is the electron transfer from the catalyst to the oxidized photosensitizer.[23] Such a process regenerates the photosensitizer and allows the accumulation of positive charges (holes) on the catalyst structure. A fast and efficient hole scavenging is needed if a regenerative photochemical catalytic system (e.g., a photoelectrosynthetic cell[25]) has to be designed. A classical experiment for determining hole scavenging rate constants is flash photolysis, in which Ru(bpy)$_3^{3+}$ is prepared by laser excitation of Ru(bpy)$_3^{2+}$, followed by irreversible oxidation of the MLCT state by persulfate anions.[23] Formation of Ru(bpy)$_3^{3+}$ is evidenced by the bleaching of the 450 nm MLCT absorption band, which, in the absence of an electron donor, is irreversible on the μs time scale (see Figure 4). In the presence of **1**, the bimolecular hole
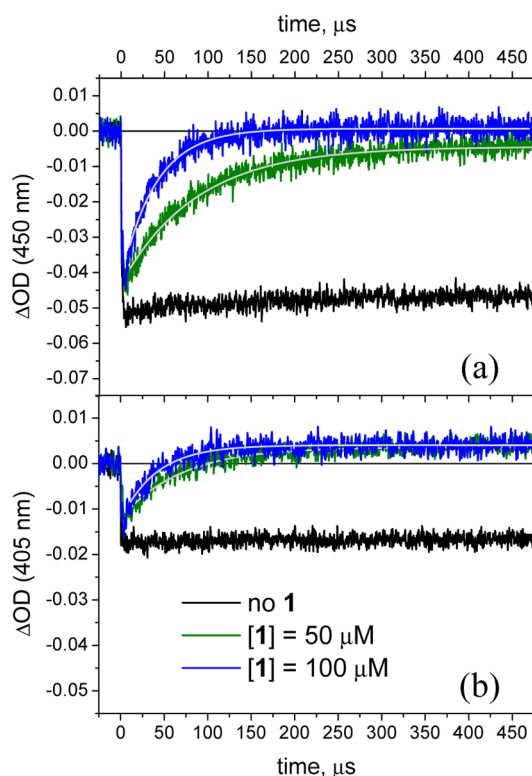
Figure 4. Flash photolysis experiments (excitation at 355 nm, fwhm 6−8 ns) of mixed 50:50 acetonitrile: 40 mM phosphate buffer (pH 7) solutions containing 50 μM Ru(bpy)$_3$Cl$_2$, 5 mM Na$_2$S$_2$O$_8$, and 0−100 μM **1**, measured (a) at 450 nm and (b) at 405 nm, with related single-exponential fitting.

scavenging process (eq 1) takes place, as indicated by the different absorbance changes observed at 450 nm (where Ru(bpy)$_3^{3+}$ and Ru(bpy)$_3^{2+}$ are the main absorbing species, and the process shows up as recovery of the initial bleach) and also at 405 nm (where the additional positive absorption is indicative[17b] of the conversion of **1** to **1**$^+$). This is the first time that the oxidation of a molecular catalyst is directly visualized and time-resolved in bimolecular systems in solution, although with limitation to the first oxidation step of the overall process.[26] Using the catalyst in excess concentration (i.e., under pseudo-first-order conditions, Figure S2), the rate constant for the hole scavenging reaction (eq 1) can be obtained as 2.5 × 10^8 M^{-1} s^{-1}. This rate constant is comparable to those obtained in similar conditions for a series of the tetracobalt(III) cubane species formerly studied,[11e] and definitely faster than that for colloidal iridium oxide,[23] known to be a good water oxidation catalyst.

$$Ru(bpy)_3^{3+} + \mathbf{1} \rightarrow Ru(bpy)_3^{2+} + \mathbf{1}^+ \qquad (1)$$
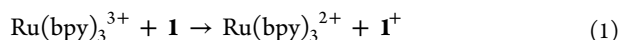
In summary, for the first time a multimetallic cluster containing vanadium atoms as the only transition metal centers has been demonstrated to play the role of a water oxidation catalyst. The photochemical quantum yield (0.20) calculated by using such a methoxo-polyoxovanadate cluster as the catalyst, using Ru(bpy)$_3^{2+}$ as the photosensitizer, and Na$_2$S$_2$O$_8$ as the sacrificial electron acceptor, in mixed solvents at 450 nm excitation, is comparable with the quantum yield values obtained for the most studied homogeneous cobalt catalysts in similar photocatalytic systems. The rate constant for hole scavenging, obtained by nanosecond flash photolysis, is 2.5 ×

10^8 M^{-1} s^{-1} and has been investigated by following both the recovery of the photosensitizer Ru(bpy)$_3^{2+}$ and the formation of the oxidized molecular catalyst **1**$^+$. Altogether, these results indicate that alkoxo-polyoxovanadium clusters are well-suited to take an active part in artificial photosynthetic schemes and are expected to stimulate further work in the search for molecular, active water oxidation catalysts made with less expensive, earth-abundant metals.

■ ASSOCIATED CONTENT

ⓢ Supporting Information
Equipment, general procedures, CV of **1** in acetonitrile, and kinetics for the calculation of the bimolecular rate constant of the hole scavenging process are reported. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Authors
*E-mail: msantoni@unime.it.
*E-mail: snf@unife.it.
*E-mail: campagna@unime.it.

Notes
The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

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