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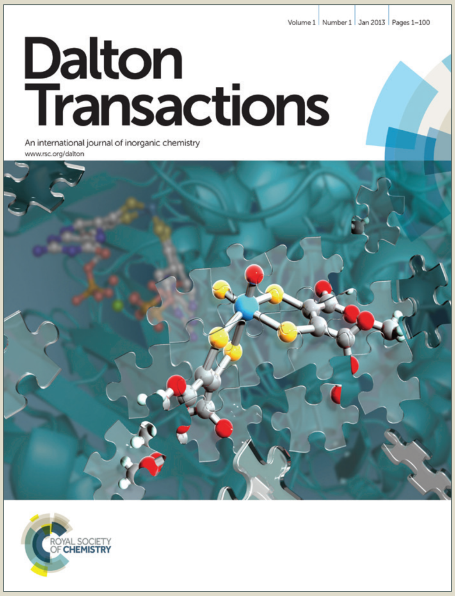

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ARTICLE TYPE

New findings and the current controversies for the water oxidation by a copper(II)-azo complex: Homogeneous or heterogeneous?†

Mohammad Mahdi Najafpour,*[ab] Foad Ebrahimi,‡[a] Rasoul Safdari,‡[a] Mohadeseh Zarei Ghobadi,‡[a] Mojtaba Tavahodi‡[a] and Parvin Rafighi‡[a]

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In this paper, new findings for the water-oxidizing activity of [(L)Cu^{II}(NO$_3$)] , (L = (*E*)-3-(pyridin-2-yldiazenyl) naphthalen-2-ol (HL)) in both electro-water oxidation condition and in the presence of cerium(IV) ammonium nitrate are reported.

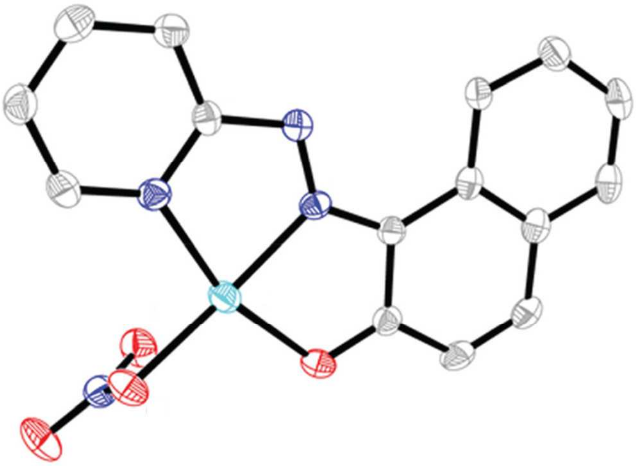
Introduction

Hydrogen is a very important carrier for the conversion of sustainable, but intermittent energies.[1,2] Electrochemical or photoelectrochemical water splitting systems are proposed for high scale H_2 production in future.[1-4] To this end, efficient light harvesting compounds, charge separators and catalysts for water oxidation/reduction are necessary.[1]

Among different reactions for water splitting, water oxidation is a bottleneck, and thus, the finding of an efficient, cheap and environmentally friendly water-oxidizing compound is highly desirable for water splitting systems.[1] Various compounds of Mn,[5-11] Fe,[12-15] Co[17,18] and Cu[19-23] have been found as promising catalysts because of the high availability and low toxicity of these metals. Mayer's group reported a homogeneous Cu complex for electrochemically driven water oxidation.[20] Although the complex has a high overpotential of ~ 0.75 V, it is robust and displayed high rates at pH 12.5.[20] Chen and Meyer reported that simple Cu(II) salts were electrochemically active in catalyzing H_2O oxidation with an overpotential of ~ 0.45 V and stability for at least 6 h at pH 10.8.[19] The group also reported Cu(II)/triglycylglycine macrocyclic complex. It shows water-oxidation activity at overpotential of ~ 0.52 V and at least 5 h stability.[21]

As a model for tyrosine 161 in photosystem II, which is near metal site, the Lin group used 6,6′-dihydroxy-2,2′-bipyridine with Cu(II) to obtain a water-oxidizing catalyst. The water oxidation by the complex was found to occur at an overpotential of ~ 510-560 mV at pH 12-14.[22]

Recently, Wei group reported [(L)Cu^{II}(NO$_3$)] (L = (E)-3-(pyridin-2-yldiazenyl)naphthalen-2-ol (HL)) (**1**) as a homogeneous catalyst for water oxidation in both electrochemical and chemical conditions (**Scheme 1**).[23]



Scheme 1 a schematic structure of **1** (O:red; C:gray; N:blue and Cu: cyan). With modification from ref. 23.

One oxygen and two nitrogen atoms from the ligand, and also one oxygen from nitrate are coordinated to Cu(II) in the structure.[23] The Wei group used pyrolytic graphite electrode used as working electrode, with Pt wire as auxiliary, and Ag/AgCl as reference electrode. From curves of CVs at pH range of 8.0-13.0 and the concentration range of 0.1-1.0 mM from the complex, they proposed that the large and irreversible oxidation peaks are related to catalytic water oxidation.[23]

On the other hand, water oxidation by **1** in the presence of Ce(IV) was reported.[23] It was also reported that a solution of **1** in methanol or acetonitrile at pH = 11 efficiently oxidizes water. [23] To design and synthesize more efficient Cu-based catalysts, the finding of true catalyst and understanding the mechanism of them for water oxidation is important. In this regard, a molecular mechanism was reported by Wei group, which shows O_2 is produced by the coupling of two [LCu(III)=O] intermediates.[23] On the other hand, **1** was reported as the true catalyst for water oxidation.[23]

Herein, we study the water-oxidizing by activity of **1** in both electrochemical and chemical condition to find more about the interesting complex and its water-oxidation reaction.

Experimental

Materials

All reagents and solvents were purchased from commercial sources and were used without further purification.

Synthesis of 1

1 (**Scheme 1**) was synthesized by previously reported method with the reaction of a solution $Cu(NO_3)_2.3H_2O$ and ligand (HL) in a 1:1 mole ratio in methanol and in a sealed vial at 60 °C.[23]

Characterization

SEM and EDX were carried out with VEGA\TESCAN-XMU. The X-ray powder patterns were recorded with a Bruker, D8 ADVANCE (Germany) diffractometer (CuK_α radiation). The infrared spectra were obtained on a FT-IR Bruker Vector spectrometer with a pressed KBr pellet. UV-Vis spectra were obtained by Pharmacia Biotech ultrospec 3100. NMR spectra were performed with a 400 MHz Brucker Avance instrument. Electrochemical experiments were performed using an EmStat^{3+} from PalmSens company (Netherlands).

Water oxidation

Oxygen evolution from aqueous solutions in the presence of cerium(IV) ammonium nitrate, $(NH_4)_2Ce(NO_3)_6$, (Ce(IV)) was measured using a HQ40d portable dissolved oxygen meter connected to an oxygen monitor with digital readout (Fig. S4, ESI†). The reactor was maintained at 25.0 ºC in a water bath. In a typical run, the instrument readout was calibrated against air-saturated distilled water stirred continually with a magnetic stirrer in the air-tight reactor. After ensuring a constant baseline reading, the water in the reactor was replaced with Ce(IV) solution. Without catalyst, Ce(IV) was stable under these conditions and oxygen evolution was not observed. After the deaeration of the Ce(IV) solution with argon, a solution of **1** was added and oxygen evolution was recorded by the oxygen meter under stirring.

Results and Discussion

The stability of 1 in water

At first, we studied the stability of complex in water.   The UV-Vis spectra of **1** in water show that the main structure of this complex is stable at least for a few hours (Fig. S1, ESI†). Cu(II) is laibile, which means the ligand exchange rate for the ion is fast. Thus, a few changes in the spectra may be related to exchange of nitrate by phosphate or water.[24a] UV-Vis spectra in H_2O at pH ~ 1 and 11 showed no significant changes for **1** in a few hours (Fig. S1, ESI†).

Because of the unfavorable electronic relaxation time for monomeric Cu(II) complexes, it is not easy to get well resolved NMR signal for these complexes.[24b] In this regards line broadening causes no well-resolved ^1H NMR signals for every individual proton of **1**, but ^1H NMR spectra in D_2O at both pH ~ 7 and 1 showed no significant changes for **1** at least after 1 hour (Fig. S2,S3, ESI†). However, ligand in the absence of Cu(II) is not stable in the presence of Ce(IV) (Fig. S2, ESI†).

The water-oxidizing activity of 1 in the presence of cerium(IV) ammonium nitrate (Ce(IV))

Ce(IV) is a commercially available, non-oxo transfer agent, one-electron, and stable oxidant. Thus, it extensively used as the primary oxidant in water oxidation catalyzed by Fe, Ru and Mn complexes.[11] It should be noted that Cl$^-$ and many organic and inorganic compounds are oxidized in the presence of Ce(IV) to form different gases.[25,26] Thus, measuring pressure or volume of produced gas is not a good method to test of oxygen evolution in the condition. We used a HQ40d portable dissolved oxygen meter to test oxygen evolution by **1** (Fig. S4, ESI†). To test water-oxidizing activity of **1**, we performed the water-oxidation experiments in the presence of Ce(IV) at pH =11 at different concentrations of **1**. However, Ce(IV) precipitates (Fig. S5, ESI†) in this condition as a yellow solid and no oxygen was observed (Fig. S5 and Fig. S6, ESI†). In the presence of Ce(IV) without buffer and at pH ~ 1, **1** is decomposed (**Fig. 1**) and no oxygen evolution was observed. In this reaction, even a decreasing in the amounts of oxygen is observed, which is related to the complex decomposition. Such the consumption of oxygen was reported by the decomposition of Mn complexes in the presence of Ce(IV).[7b]

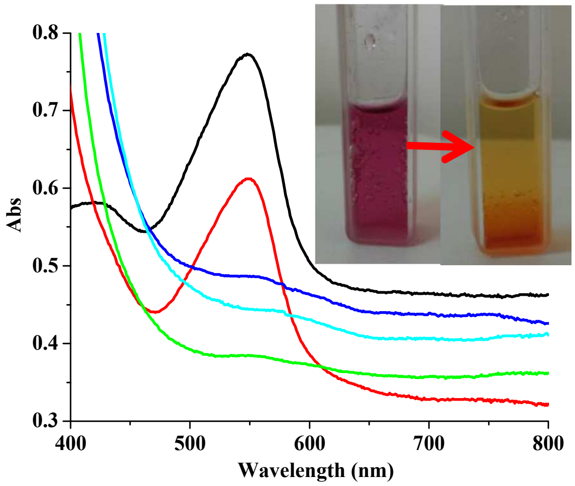


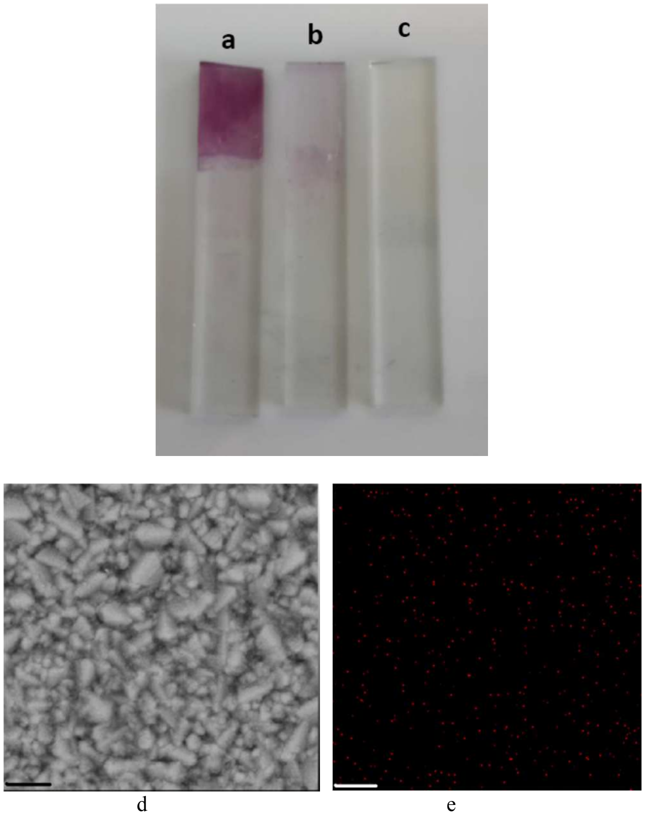
Fig. 1 The visible spectra for the titration of **1** (2.25 mL, 1.2 M) (black) with 50 (red), 100 (green), 150 (blue) and 200 µL (cyan) of Ce(IV) (0.9 M). The pictogram shows that **1** (2.25 mL, 1.2 M) at pH = 1 after adding only 100 µL Ce(IV) (0.9 M) is immediately decomposed.

The ^1H NMR of the soluble section of the solid shows that the ligand, ((*E*)-3-(pyridin-2-yldiazenyl)naphthalen-2-ol), in the complex is decomposed to other compounds without aromatic groups. In this condition, the FTIR spectrum for **1** after treatment by Ce(IV) shows new peaks related to the decomposition of ligand (Fig. S7 and S8, ESI†). Such changes are observed in the -N=N- area (1400-1600 cm^{-1}), which shows this functional group is reactive toward oxidation in the presence of Ce(IV) (Fig. S7 and S8, ESI†). The related area of Cu-N/O (400-600 cm^{-1}) also shows that lower amounts of Cu(II) ions are in **1** after treatment by Ce(IV). Elemental analysis from **1** after treatment by Ce(IV) shows more carbon, nitrogen and hydrogen than **1**. All these experiments show that after treatment of **1** by Ce(IV), ligand is decomposed and Cu(II) releases to the solution. In this condition an amorphous solid is formed, which is related to decomposed ligands (Fig. S9, ESI†). In high concentrations of Ce(IV) as a powerful oxidant and in an acidic condition, such deep oxidation of ligand is usual.[25a,b,7b] In this condition as Pourbaix diagram shows, Cu(II) cannot precipitate as CuO or Cu_2O. Although, our experiments showed that in this condition, CuO even in nano-scale size, average particle size < 50 nm and specific surface area 80 m^2/g, is not a good catalyst for water oxidation (Fig. S10, ESI†).#

The electro-water oxidation activity of 1

CuO at pH ~ 9-13 is an efficient water-oxidizing catalyst toward water oxidation.[28] To find out the true catalyst for water oxidation in the presence of **1** at pH = 11, the bulk electrolysis of **1** at ~ 1.2 V (vs. Ag|AgCl|KCl_{sat}) was performed with Fluorine doped Tin Oxide (FTO) and Pt wire as working and auxiliary electrode respectively. It is important to note that as Nocera's group demonstrated, glassy carbon electrode is decomposed under water oxidation and should be used with caution for the study of water oxidation.[27] Interestingly, for **1** in this condition a film was appeared on the FTO electrode during 6 h in the bulk electrolysis at 1.2 V (vs. Ag|AgCl|KCl_{sat}). The light gray film after washing with water and removing **1** was characterized by scanning electron microscopy, energy-dispersive X-ray analysis and X-ray diffraction.

As shown in **Fig. 2**, the SEM images of the film show nano-sized particles of SnO_2 from FTO. The EDX data shows that the obtained film at pH = 11 contains O and Sn with low amounts of Cu, C and N in which Cu is resulted from the decomposition of **1** on the surface of electrode. XRD only shows FTO and sodium phosphate from buffer (Fig. S11, ESI†). It is not surprising that SnO_2, (Fig. S12, ESI†), with a nano-sized structure absorbs **1** on its surface at least by electrostatic interaction (**Fig. 2**). Such attachments convert homogeneous catalyst to heterogeneous one and most probably decompose a Cu complex to a Cu oxide with low amounts of C and N (**Fig. 2**). Cu oxide on FTO electrode in this condition is an efficient catalyst toward water oxidation.[28]



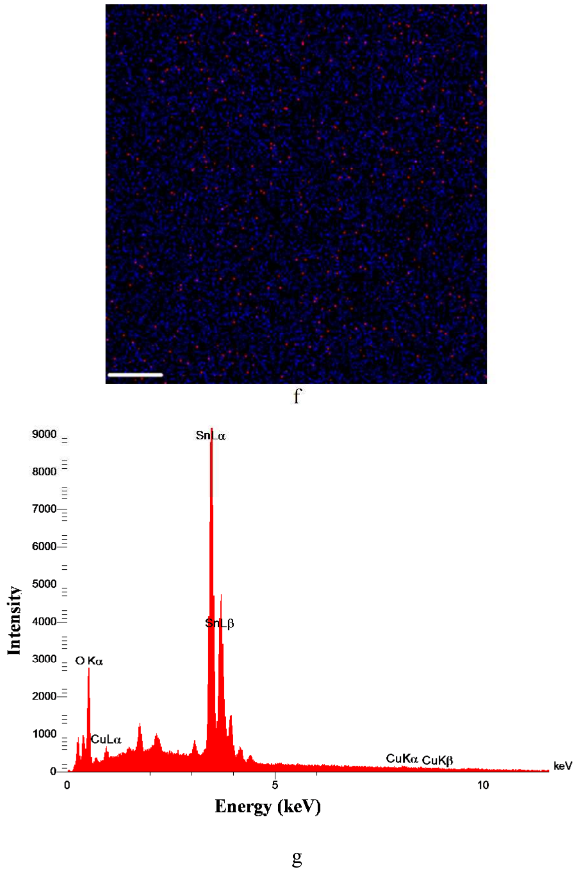


Fig. 2 Photograph from FTO electrode after 6 hours at 1.2 V (vs. Ag|AgCl|KCl_{sat}) (a) after washing with water to remove **1** from the film (b), and a clean FTO electrode (c). SEM (d) and EDX-Mapping of Cu (e) and Cu (red) or Sn (blue) (f) for appeared film on the FTO electrode during 1 h in the bulk electrolysis of **1** at 1.2 V (vs. Ag|AgCl|KCl_{sat}). The scale bar is 200 nm. EDX for b shows points with a few amounts of copper (g).

Fig. 3a presents Cyclic Voltammograms (CVs) of FTO and FTO/**1** (see **Fig. 2b**) in buffer solution at a scan rate of 50 mV s^{-1}. The large and irreversible oxidation peak in +0.84 V (vs. Ag|AgCl|KCl_{sat}), corresponding to catalytic water oxidation was clearly observed, which was related to Cu oxide layer film at the surface of FTO/**1** electrode (see Fig. 2b). Interestingly, such potential peak is comparable to water oxidation by CuO reported by Sun group.[28]

The stability of Cu oxide layer film was examined by consecutive cyclic voltammetry and long-term usage for FTO/**1** (see Fig. 2b). Faradaic efficiency for the catalyst in this condition as Yu et. al. reported is high and more than 95%.[23] Recycling potential in the range between +0.5 and +1.5 V (vs. Ag|AgCl|KCl_{sat}) with a scan rate of 50 mV s^{-1} for 40 cycles in a N_2-saturated in phosphate buffer (0.1 M, pH = 11.0) causes no significant decrease in voltammetric currents, but after holding the electrode in a N_2-saturated phosphate buffer for 10 hours, its water-oxidation current decreased dramatically (Fig. 3b). Such decreasing in water oxidation was observed in chronoamperometry (Fig. 3c). These results may be related to the weakly attached CuO or decomposed complex on the surface of the electrode.

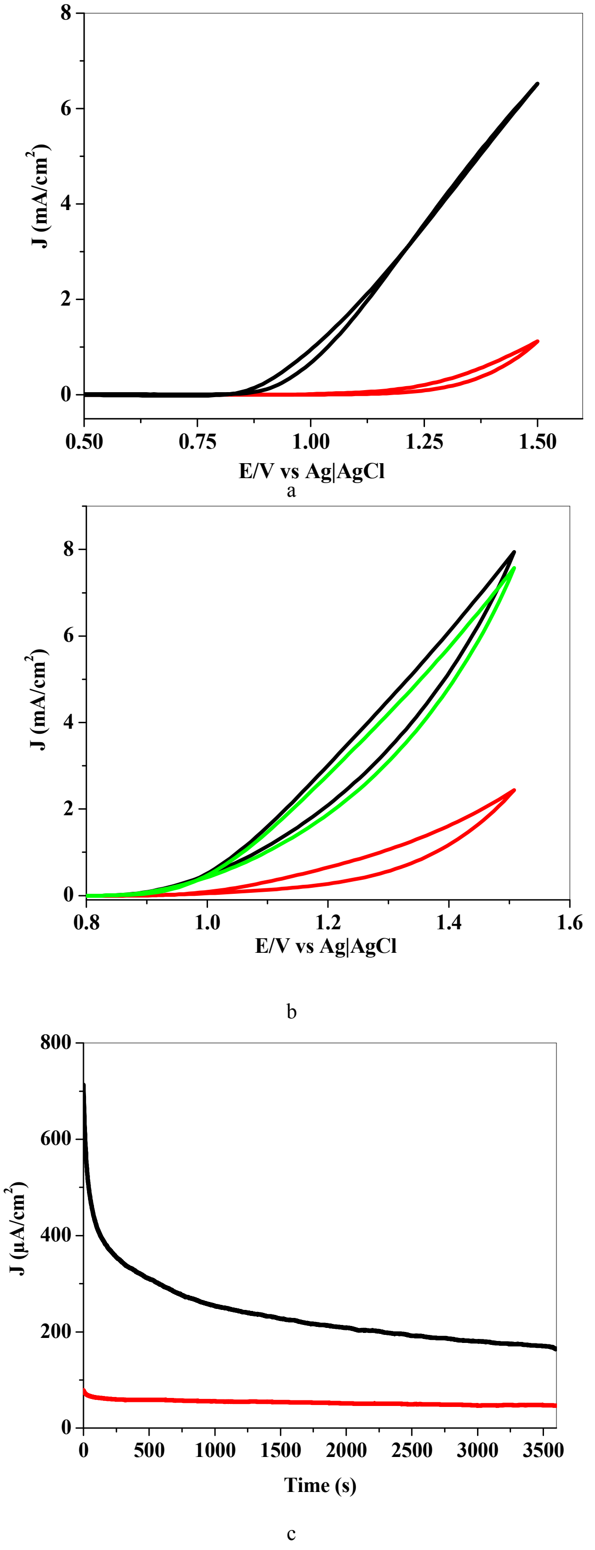
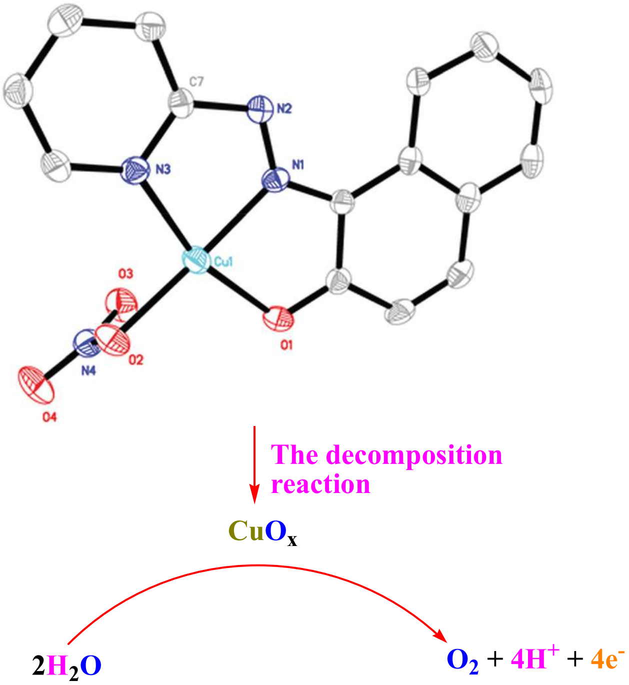


Fig. 3 Cyclic voltammograms for a clean FTO electrode, see **Fig. 2c**, (red) and FTO/**1** electrodes, see **Fig. 2b**, (black) in 0.1 M phosphate buffer (pH = 11.0) at a scan rate of 50 mVs^{-1} (a). Recycling potential in the range between +0.5 and +1.5 V (vs. Ag|AgCl|KCl$_{sat}$) for FTO/**1** electrodes (black), after 40 cycles (green) and after holding the electrode in solution for 10 hours (red) (b). Chronoamperometry for FTO (red) and FTO/**1** (black) electrodes, see **Fig. 2b**, in a N_2-saturated phosphate buffer (1.2 vs. Ag|AgCl|KClsat) (c). Cyclic voltammetry studies were carried out with a conventional three-electrode setup, in which a FTO, an Ag|AgCl|KCl$_{sat}$ and a platinum rod served as the working, reference and auxiliary electrodes, respectively. The phosphate buffer solution (0.1 M, pH = 11) has been deoxygenated with pure N_2 in order to the removal of dissolved oxygen from the sample solution.

These documents clearly show that a heterogeneous catalyst is responsible for water oxidation in this electrochemical condition (**Scheme 2**) and we propose that the water oxidation in the condition is oxide-based. Such mechanisms are possible for many metal complexes in the water-oxidation condition because ligands usually are not stable in the oxidizing-condition related to water oxidation. In this condition, metal ions from the metal complexes release to solution after the ligand decomposition and form nano-sized metal oxides in the presence of oxidant. The surface of the electrode, similar to clay,[7b] can strongly bind to the product of decomposition of metal complexes and form a metal oxide that could oxidize water.



Scheme 2 The proposed mechanism for water oxidation by **1**.

All these experiments indicate:

- Measuring the pressure or volume of producing gas is not a good method to test of oxygen evolution in the presence of a complex and Ce(IV) because in this condition other gases except oxygen such as CO_2, Cl_2 and so on may be formed.
- In the reaction of metal complex with Ce(IV), the true catalyst should be carefully checked because usually the acidic and oxidizing conditions decompose ligands in the complexes.[29]
- For water oxidation by metal complexes in electrochemical condition, the precipitation of metal oxides in water oxidation should be carefully checked because such metal oxides can form film on the surface of the electrode. Such film is active in water oxidation.[29]
- As many organic ligands with different metal ions in the presence of strong reductants and oxidants were extensively used as catalysts toward different oxidation and reduction reactions,

careful analyses should be considered to detect true catalysts.[30]

Conclusions

We considered the water-oxidizing activity of a copper complex with (*E*)-3-(pyridin-2-yldiazenyl)naphthalen-2-ol as ligand.

We observed no oxygen evolution from this complex in the presence of Ce(IV) at pH = 1 and 11. Electro-water oxidation at pH = 11 is observed, which is related to Cu oxide formation. We propose that to find true catalyst in related condition, the stability of metal complex in the water-oxidation and other oxidation/reduction condition should be carefully checked because in these conditions organic ligands are usually decomposed and metal ions form nano-sized metal oxides, which are efficient catalysts toward water oxidation.

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Notes and references

[a] *Department of Chemistry, Institute for Advanced Studies in Basic Sciences (IASBS), Zanjan, 45137-66731, Iran*
[b] *Center of Climate Change and Global Warming, Institute for Advanced Studies in Basic Sciences (IASBS), Zanjan, 45137-66731, Iran*
**Corresponding author:*
Phone: (+98) 24 3315 3201. E-mail: mmnajafpour@iasbs.ac.ir

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‡ *These authors contributed equally to the work.*

#It is possible that other phases from Cu oxides in this condition efficiently catalyze water oxidation. However, it is important that ***1*** *does not oxidize water in this condition.*

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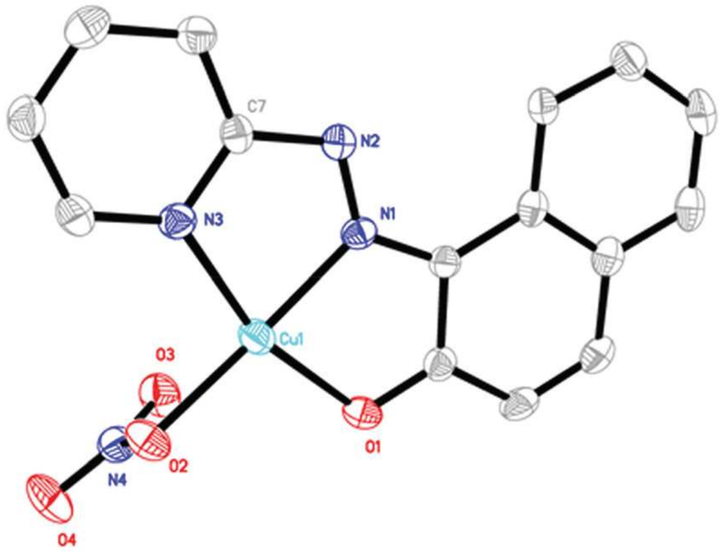
New findings for the water-oxidizing activity of [(L)Cu^{II}(NO$_3$)] , (L = (*E*)-3-(pyridin-2-yldiazenyl) naphthalen-2-ol (HL)) in both electro-water oxidation condition and in the presence of cerium(IV) ammonium nitrate are reported.



$$2H_2O \rightarrow O_2 + 4H^+ + 4e^-$$

Homogeneous or heterogeneous