ChemComm

Heterogeneous Catalytic Water Oxidation Controlled by Coordination Geometries of Copper(II) Centers with Thiolato Donors

ChemComm

COMMUNICATION

Heterogeneous Catalytic Water Oxidation Controlled by Coordination Geometries of Copper(II) Centers with Thiolato Donors

Naoto Kuwamura,[a] Yoshinari Kurioka,[a] Nobuto Yoshinari,[a] and Takumi Konno[a]*

Treatment of a penicillaminato platinum(II) metalloligand with Cu^{2+} gave an *S*-bridged $Pt^{II}_2Cu^{II}_2$ complex, which reacted with Zn^{2+} to produce 1D and 3D $(Pt^{II}_2Cu^{II}_2Zn^{II})_n$ coordination polymers dependent on counter anions. These compounds increased heterogeneous electrocatalytic activities for water oxidation in proportion to the number of vacant coordination sites at thiolato dicopper(II) cores.

The catalytic splitting of water into hydrogen and oxygen is an important subject in not only inorganic chemistry but also green chemistry due to the globally increasing demand for sustainable energy.[1] Of the two water-splitting half-reactions, water oxidation is more difficult because four electrons and four protons are required for O–O bond formation.[2] Progress in 'homogeneous' catalytic water oxidation has been achieved in the last decade, initially with Ru and Ir coordination compounds, and later with coordination compounds of the first transition metals.[3–5] On the other hand, 'heterogeneous' catalysts for water oxidation have not been developed, despite their potential advantages of durability and recyclability compared with homogeneous catalysts. In particular, heterogeneous activities toward water oxidation have rarely been investigated for copper compounds,[6] although their homogeneous catalysis properties have attracted considerable attention because of their rich redox chemistry and relevance to biological systems.[5]

In general, amido/imine ligands with nitrogen donor(s) and/or alkoxide ligands with oxygen donor(s) are employed in water oxidation catalysts because these ligands can stabilize the high oxidation states of metal centers and are stable during catalytic redox cycles.[3–5] It has been recognized that thiolate ligands also have the ability to stabilize the high oxidation states of metal centers such as Cu^{III} and Ni^{IV}.[7] However, no reports have described the use of thiolato coordination compounds as water oxidation catalysts, presumably because of the facile oxidation of the thiolato groups in the course of the catalytic reactions. We have been studying the coordination behavior of metal complexes with thiolate ligands, which can function as *S*-donating metalloligands to form a variety of *S*-bridged polynuclear and supramolecular coordination compounds.[8–10] This class of compounds is fairly stable toward oxidation because each thiolato group is bound by two metal centers. Recently, we reported that a linear-type platinum(II) complex with D-penicillaminate (D-pen), *trans*-$[Pt(NH_3)_2(D\text{-}pen\text{-}S)_2]^{2-}$ (D-$[1]^{2-}$), acted as a multifunctional metalloligand to afford a $(Pt^{II}_2Pd^{II}_2Ni^{II})_n$ heterotrimetallic coordination polymer by way of an *S*-bridged $Pt^{II}_2Pd^{II}_2$ heterobimetallic tetranuclear complex. The $(Pt^{II}_2Pd^{II}_2Ni^{II})_n$ coordination polymer showed enhanced heterogeneous electrocatalytic activity for hydrogen evolution without any side reactions.[11] This was ascribed to the increase of Lewis acidity around the Pd^{II} catalytic center in the $[Pd^{II}(amine)_2(thiolato)_2]$ square plane due to the binding to the Ni^{II} center through a D-pen carboxylate group. Prompted by this result, in this study, we employed the metalloligand $[1]^{2-}$ in the preparation of $(Pt^{II}_2Cu^{II}_2Zn^{II})_n$ coordination polymers ($[3]$Cl and $[4](ClO_4)_2$) composed of *S*-bridged $Pt^{II}_2Cu^{II}_2$ tetranuclear units, by way of a $Pt^{II}_2Cu^{II}_2$ tetranuclear complex ($[2]$) (Scheme 1). Importantly, the $Pt^{II}_2Cu^{II}_2$ tetranuclear units in $[2]$, $[3]$Cl, and $[4](ClO_4)_2$ contain two Cu^{II} centers with different coordination geometries, which leads to different heterogeneous electrocatalytic activities toward water oxidation. These are the first thiolato copper(II) species that show appreciable catalytic water-oxidation activity.

[a.] Department of Chemistry, Graduate School of Science, Osaka University, Toyonaka, Osaka 560-0043
E-mail: konno@chem.sci.osaka-u.ac.jp

† Electronic Supplementary Information (ESI) available: Synthesis, IR, ESI-MS, diffuse reflection, LSV, GC, crystal packing. See DOI: 10.1039/x0xx00000x
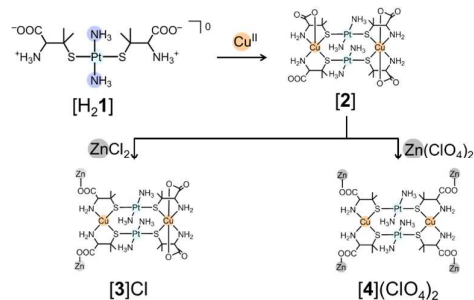
Scheme 1. Synthetic route to [**3**]$^+$ and [**4**]$^{2+}$ via [**1**]$^{2-}$ and [**2**].

The reaction of an aqueous white suspension of [Pt(NH$_3$)$_2$(D-Hpen-*S*)$_2$] (D-[H$_2$**1**]) with Cu(OAc)$_2$ in a 1:1 ratio in air gave a black solution, from which a black powder ([**2**]) was isolated in high yield. X-ray fluorescence spectroscopy indicated that [**2**] contains Pt and Cu, and the elemental analytical data were consistent with the formula for a 1:1 adduct of [**1**]$^{2-}$ and Cu^{2+}. The presence of deprotonated carboxyl groups in [**2**] was confirmed by its IR spectrum, which shows a broad absorption band at 1587 cm^{-1} (Figure S1, ESI†).[12] From these results, [**2**] is assigned to the expected Pt$^{II}_2$Cu$^{II}_2$ tetranuclear structure in [Cu$_2${Pt(NH$_3$)$_2$(D-pen)$_2$}$_2$], analogous to the previously reported [Pd$_2${Pt(NH$_3$)$_2$(D-pen)$_2$}$_2$].[11] This assumption is supported by the ESI-TOF-mass spectrum of [**2**], which displayed a dominant signal at *m/z* 1197 corresponding to [Cu$_2${Pt(NH$_3$)$_2$(pen)$_2$}$_2$ + Na]$^+$ (Figure S2, ESI†). A similar reaction using a racemic 1:1 mixture of D-[H$_2$**1**] and L-[H$_2$**1**] also afforded a black product that was assigned to the racemate [**2'**], consisting of [**2**] and its enantiomer in a 1:1 ratio, based on the X-ray fluorescence, IR, ESI-TOF-mass spectra, and elemental analysis. The solid-state diffuse reflection spectrum of [**2'**] is the same as that of [**2**], which also supports this assignment (Figure S3, ESI†). While all attempts to isolate single crystals of [**2**] suitable for X-ray crystallography were unsuccessful, we could obtain single crystals of [**2'**]. X-ray analysis revealed the presence of a pair of enantiomeric molecules ([**2**] and its enantiomer), besides water molecules of crystallization, in the asymmetric unit.[14] As shown in Figure 1, [**2**] has the expected Pt$^{II}_2$Cu$^{II}_2$ tetranuclear structure in [Cu$_2${Pt(NH$_3$)$_2$(D-pen)$_2$}$_2$], in which two D-[**1**]$^{2-}$ metalloligands bridge two Cu^{II} atoms. While the two D-pen moieties of one metalloligand coordinate to Cu^{II} centers in a tridentate-*N,O,S* mode, those of the other metalloligand coordinate to Cu^{II} centers in bidentate-*N,S* and tridentate-*N,O,S* modes. As a result, one Cu^{II} center is situated in an octahedral (*OC*-6) geometry with two carboxylato-*O* donors at the apical positions of a *cis*(N)·*cis*(S) square plane, while the other Cu^{II} center lies in a square-pyramidal (*SPY*-5) geometry with an *O* donor at the apical position of a *cis*(N)·*cis*(S) square plane. In the crystal, each [**2**] unit is hydrogen-bonded with four enantiomeric molecules through amine and carboxylate groups (av. N$_{pen}$···O = 3.05 Å), constructing a 3D hydrogen-bonded network structure (Figure S4, ESI†).

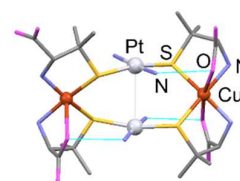**Fig. 1.** Molecular structure of [**2**] in [**2'**]. The Pt···Pt distance is 3.231(1) Å, which is suggestive of the presence of a weak Pt···Pt interaction.[14] Three of four NH$_3$ groups each form an intramolecular hydrogen bond with a carboxylato-*O* donor (av. N$_{NH3}$···O = 3.05 Å).

To investigate the reactivity of the carboxylate groups in [**2**], we treated D-[**2**] with ZnCl$_2$ (1:1) in water under aerobic conditions, which produced X-ray-quality black prism-shaped crystals ([**3**]Cl). This product was assigned to a 1:1 adduct of [**2**] and ZnCl$_2$ based on the fluorescence X-ray and elemental analyses, together with the IR spectrum (Figure S1, ESI†).[12] Single-crystal X-ray diffraction analysis revealed that [**3**]Cl is composed of the Pt$^{II}_2$Cu$^{II}_2$ units of [**2**] (Figure 2), which are alternately linked by [ZnCl(H$_2$O)]$^+$ units in a (Pt$^{II}_2$Cu$^{II}_2$Zn^{II})$_n$ chain structure through COO–Zn bonds, in addition to Cl$^-$ counter anions and water molecules of crystallization.[13] One of two Cu^{II} centers in each Pt$^{II}_2$Cu$^{II}_2$ molecule adopts an octahedral (*OC*-6) geometry with two carboxylato groups binding at the apical positions of a *cis*(N)·*cis*(S) Cu^{II} square plane. The other Cu^{II} center has a *cis*(N)·*cis*(S) square-planar (*SP*-4) geometry, with two carboxylate groups each binding to a [ZnCl(H$_2$O)]$^+$ unit. Each bridging Zn^{II} center is situated in a tetrahedral geometry bound by two carboxylate groups from two Pt$^{II}_2$Cu$^{II}_2$ units (av. Zn–O = 1.96 Å), in addition to a chloride ion and a water molecule.
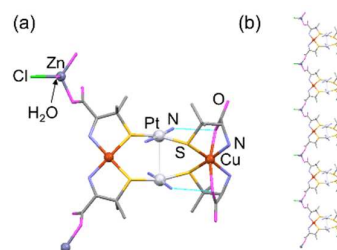

Fig. 2. (a) Molecular structure of the Pt$^{II}_2$Cu$^{II}_2$Zn^{II} unit in [**3**]$^+$ and (b) the 1D chain structure. The intramolecular Pt···Pt distance is 3.198(1) Å. Two of four NH$_3$ groups each form an intramolecular hydrogen bond with a carboxylato-*O* donor (av. N$_{NH3}$···O = 2.98 Å).

We next performed a similar 1:1 reaction of [**2**] using Zn(ClO$_4$)$_2$ instead of ZnCl$_2$, which gave black needle crystals ([**4**](ClO$_4$)$_2$). From the X-ray fluorescence and elemental analyses, together with the IR spectrum, this product was assigned to a 1:1 adduct of [**2**] and Zn(ClO$_4$)$_2$, as in the case of [**3**]Cl. However, X-ray analysis established that [**4**](ClO$_4$)$_2$ does not have a 1D (Pt$^{II}_2$Cu$^{II}_2$Zn^{II})$_n$ chain structure, but rather a 3D (Pt$^{II}_2$Cu$^{II}_2$Zn^{II})$_n$ structure in which the Pt$^{II}_2$Cu$^{II}_2$ tetranuclear units are each linked by four Zn^{II} atoms through four carboxylate groups (Figure 3).[13] Both Cu^{II} centers in each Pt$^{II}_2$Cu$^{II}_2$ unit have a *cis*(N)·*cis*(S) square-planar (*SP*-4) geometry, with four carboxylate groups each coordinating to a Zn^{II} atom.[15] The

bridging Zn^{II} centers in [**4**](ClO_4)$_2$ are each situated in a tetrahedral geometry bound by four carboxylate groups from the four $Pt^{II}_2Cu^{II}_2$ units (av. Zn–O = 1.96 Å). Perchlorate ions are not involved in the coordination and are accommodated in the cationic ($Pt^{II}_2Cu^{II}_2Zn^{II}$)$_n$ framework via N–H⋯O hydrogen bonds with NH_3 groups (av. N_{NH3}⋯O = 3.19 Å). Thus, the poor coordination ability of perchlorate ion leads to the coordination of all four carboxylate groups in each $Pt^{II}_2Cu^{II}_2$ unit to Zn^{II} centers to construct the 3D ($Pt^{II}_2Cu^{II}_2Zn^{II}$)$_n$ coordination framework. Such a drastic change in dimensional structure controlled by counter anions is noteworthy.
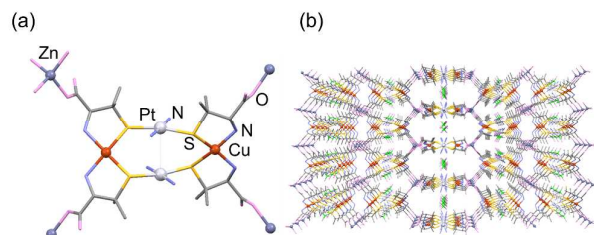

Fig. 3. (a) Molecular structure of the $Pt^{II}_2Cu^{II}_2Zn^{II}$ unit in [**4**]$^{2+}$ and (b) the 3D network structure. The intramolecular Pt⋯Pt distance is 3.202(1) Å.
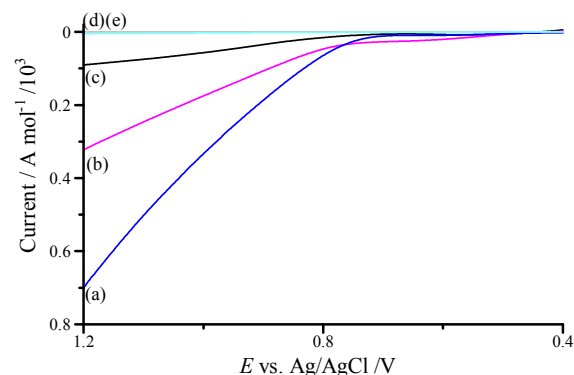
Fig. 4. Linear sweep voltammograms of (a) [**4**](ClO_4)$_2$-, (b) [**3**]Cl-, (c) [**2**]-, (d) [H_2**1**]-modified glassy carbon electrodes (0.07 cm^2), and (e) a bare glassy carbon electrode, in H_2O-CH_3CN (v/v = 1/4) containing 0.1 M KPF$_6$. The scan rate is 10 mV/sec.

The catalytic properties of [**2**], [**3**]Cl, and [**4**](ClO_4)$_2$ in the solid state were examined by voltammetry at room temperature. Linear sweep voltammograms were recorded with sample-modified glassy carbon electrodes in CH_3CN-H_2O (4:1) containing 0.1 M KPF$_6$. As shown in Figure 4, the compounds exhibit current increases with increasing potentials in the order [**2**] < [**3**]Cl < [**4**](ClO_4)$_2$ starting at an onset potential of ca. +0.75 V (vs. Ag/AgCl). When absolute CH_3CN is used as the solvent instead of H_2O/CH_3CN, the current increase is not observed (Figure S5, ESI†). Thus, this phenomenon is a result of electrocatalytic water oxidation. Since a similar water oxidation catalytic activity was not observed for [H_2**1**] (Figure 4d) and the previously reported [Pd$_2${Pt(NH_3)$_2$(D-pen)$_2$}$_2$] (Figure S6, ESI†), we concluded that the water oxidations for [**2**], [**3**]Cl, and [**4**](ClO_4)$_2$ occur at Cu^{II} centers. In addition, copper(II) oxide, a known water-oxidation catalyst, does not produce a catalytic current under the same conditions (CH_3CN-

H_2O, Figure S7, ESI†), indicating that the observed catalysis does not originate through compound decomposition.[16] The overpotential evaluated for [**2**], [**3**]Cl, and [**4**](ClO_4)$_2$ is 133 mV, based on an onset potential of +0.75 V (vs. Ag/AgCl) at pH ~7. This value is appreciably lower than that observed for the homogeneous copper(II) catalyst (170 mV), which is the lowest water oxidation overpotential at room temperature so far reported (Table S2, ESI†).[17]

Potential-controlled electrolyses at an applied potential of +1.20 V (vs. Ag/AgCl) revealed that the rates of Coulomb charge increase in the order [**2**] < [**3**]Cl < [**4**](ClO_4)$_2$, in parallel with the voltammetric results (Figure S8, ESI†). During the electrolyses, the generation of O_2 gas was detected using gas chromatography for [**3**]Cl and [**4**](ClO_4)$_2$ (Figure S9, ESI†). The turnover frequencies (TOF) were calculated to be 4.2, 18, and 27 h^{-1} for [**2**], [**3**]Cl and [**4**](ClO_4)$_2$, respectively. The GC analysis indicated that the amount of O_2 gas generated during the electrolysis using [**3**]Cl and [**4**](ClO_4)$_2$ was 0.46 μmol and 0.67 μmol, respectively (Figure S9, ESI†). From these values, the Faraday efficiencies for [**3**]Cl and [**4**](ClO_4)$_2$ were calculated to be 15% and 86%, respectively, indicating that [**3**](ClO_4)$_2$ is fairly stable during the electrolysis. It has been proposed that catalytic water oxidation is initiated with the oxidation of a copper(II) center, accompanied by water coordination.[5h,18] This might be also the case for [**2**], [**3**]Cl, and [**4**](ClO_4)$_2$ because an oxidation wave appears near +0.47 V (vs. Ag/AgCl) for each compound, prior to the catalytic current increase (Figure S10, ESI†). In the present system, the increasing TOF values (in the order [**2**] < [**3**]Cl < [**4**](ClO_4)$_2$) parallel the rising number of vacant coordination sites (n), [**2**] (n = 1) < [**3**]Cl (n = 2) < [**4**](ClO_4) (n = 4), clearly indicating the importance of vacant coordination sites around the Cu^{II} centers for water coordination.[19] Two mechanisms—single-site and two-site—have been proposed for water oxidation.[3b] The former is much more probable for the present cases, considering the large separations between Cu^{II} centers in D-[**2**], D-[**3**]Cl and D-[**4**](ClO_4)$_2$.

In summary, we have shown that the penicillaminato platinum(II) complex ([**1**]$^{2-}$) serves as a multidentate metalloligand for Cu^{2+} ions, forming an S-bridged $Pt^{II}_2Cu^{II}_2$ tetranuclear complex ([**2**]) in aqueous media without any redox reactions between the thiolato groups and Cu^{2+} ions. The presence of carboxylate groups in [**2**] allows it to further react with Zn^{2+} ions to produce 1D and 3D ($Pt^{II}_2Cu^{II}_2Zn^{II}$)$_n$ heterotrimetallic coordination polymers ([**3**]Cl and [**4**](ClO_4)$_2$), dependent on the coordination ability of the counter anions (Cl^- vs ClO_4^-). Thanks to the flexible nature of the coordination geometries for the Cu^{II} centers, [**2**], [**3**]Cl, and [**4**](ClO_4)$_2$ form S-bridged dicopper(II) cores with different coordination geometries, *OC-SPY*, *OC-SP*, and *SP-SP*, respectively. Remarkably, these heterometallic compounds display the ability to electrocatalytically oxidize water, which increases linearly in the order [**2**], [**3**]Cl, and [**4**](ClO_4)$_2$, in parallel with the numbers of vacant coordination sites at the dicopper(II) cores. These are the first coordination systems that demonstrate a clear correlation between catalytic activity and metal coordination sites at the molecular level, as well as

catalytic activity for water oxidation due to copper(II) species with thiolato donors. Further investigation on the design of new catalysts using other metalloligands is currently underway in our laboratory.

Notes and references

1   (a) W. J. Youngblood, S.-H. A. Lee, K. Maeda, and T. E. Mallouk, *Acc. Chem. Res*. **2009**, *42*, 1966-1973; (b) T. R. Cook, D. K. Dogutan, S. Y. Reece, Y. Surendranath, T. S. Teets, and D. G. Nocera, *Chem. Rev.* **2010**, *110*, 6474-6502; (c) D. Kim, K. K. Sakimoto, D. Hong, and P. Yang, *Angew. Chem. Int. Ed.* **2015**, *54*, 3259-3266.
2   (a) X. Wu, F. Li, B. Zhang, and L. Sun, J. *Photochem. Photobiol. C,* **2015**, *25*, 71-89; (b) M. D. Karkas, and B. Akermark, *Dalton Trans.* **2016**, *45*, 14421-14461.
3   (a) N. D. Schley, J. D. Blakemore, N. K. Subbaiyan, C. D. Incarvito, F. D'Souza, R. H. Crabtree, and G. W. Brudvig, *J. Am. Chem. Soc.* **2011**, *133*, 10473-10481; (b) D. W. Shaffer, Y. Xie, and J. J. Concepcion, *Chem*. *Soc*. *Rev.* **2017**, *46*, 6170-6193.
4   (a) M. A. Asraf, H. A. Younus, M. Yusubov, and F. Berpoort, *Catal. Sci. Technol.* **2015**, *5*, 4901-4925; (b) B. M. Hunter, H. B. Gray, and A. M. Müller, *Chem*. *Rev.* **2016**, *116*, 14120-14136; (c) M. D. Kärkäs, and B. Åkermark, *Dalton Trans*. **2016**, *45*, 14421-14461.
5   (a) S. M. Barnett, K. I. Goldberg, and J. M. Meyer, *Nat. Chem.* **2012**, *4*, 498-502; (b) M.-T. Zhang, Z. Chen. P. Kang, and T. J. Meyer, *J. Am. Chem. Soc.* **2013**, *135*, 2048-2051; (c) Z. Chen., and T. J. Meyer, *Angew. Chem. Int. Ed.* **2013**, *52*, 700-703; (d) X.-J. Su, M. Gao, L. Jaio, T.-Z. Liao, P. E. M. Siegbahn, J.-P. Cheng, and M.-T. Zhang, *Angew. Chem. Int. Ed.* **2015**, *54*, 4909-4914; (e) J. Shen, M. Wang, P. Zhang, J. Jiang, and L. Sun, *Chem. Commun.* **2017**, *53*, 4374-4377; (f) L. A, Stott, K. E. Prosser, E. K. Berdichevsky, C. J. Walsby, and J. J. Warren, *Chem. Commun.* **2017**, *53*, 651-654; (g) K. J. Fisher, K. L. Materna, B. Q. Mercado, R. H. Crabtree, and G. W. Brudvig, *ACS Catal.* **2017**, *7*, 3384-3387; (h) S. J. Koepke, K. M. Light, P. E. VanNatta, K. M. Wiley, and M. T. Kieber-Emmons, *J. Am. Chem. Soc.* **2017**, *139*, 8586-8600; (i) J. Shen, M. Wang, J. Gao, H. Han, H. Liu, and L. Sun, *ChemSusChem*, **2017**, *10*, 4581-4588; (j) M.-C. Kafentzi *et al.*, *Chem. Eur. J.* **2018**, *24*, 5213-5224.
6   The only example reported thus far is a mononuclear copper(II) complex with nitrogen donor atoms, which was heterogenized on a graphene sheet: P. Garrido-Barros, C. Gimbert-Suriñach, D. Moonsirm, A. Picón, P. Monge, V. S. Batista, and A. Llobet, *J. Am. Chem. Soc.* **2017**, *139*, 12907-12910.
7   (a) J. Hanss, and H.-J. Krüger, *Angew. Chem. Int. Ed.*, **1996**, *35*, 2827-2830; (b) E. C. M. Ording-Wenkaer, M. A. Siefier, M. Lutz, and E. Bouwman, *Inorg. Chem.* **2013**, *52*, 13113-13122; (c) M. Kouno, N. Yoshinari, N. Kuwamura, K. Yamagami, A. Sekiyama, M. Okumura, and T. Konno, *Angew. Chem., Int. Ed.* **2017**, *56*, 13762-13766.
8   (a) T. Konno, *Bull. Chem*. *Soc. Jpn*. **2004**, *77*, 627-649; (b) A. Igashira-Kamiyama, and T. Konno, *Dalton Trans*. **2011**, *40*, 7249-7263; (c) N. Yoshinari, and T. Konno, *Chem. Rec.* **2016**, *16*, 1647-1663; (d) N. Yoshinari, and T. Konno, *Bull. Chem. Soc. Jpn.* **2018**, *91*, 790-812.
9   (a) A. Toyota, T. Yamaguchi, A. Igashira-Kamiyama, T. Kawamoto, and T. Konno, *Angew. Chem., Int. Ed.* **2005**, *44*, 1088-1092; (b) M. Taguchi, A. Igashira-Kamiyama, T. Kajiwara, and T. Konno, *Angew. Chem., Int. Ed.* **2007**, *46*, 2422-2425; (c)

Y. Sameshima, N. Yoshinari, K. Tusge, A. Igashira-Kamiyama, and T. Konno, *Angew. Chem. Int. Ed.* **2009**, *48*, 8469-8472; (d) A. Igashira-Kamiyama, A. Fukushima, and T. Konno, *Chem. Eur. J.* **2013**, *19*, 16532-16536; (e) S. Surinwong, N. Yoshinari, B. Yotnoi, and T. Konno, *Chem. Asian J.* **2016**, *11*, 486-490; (f) S. Surinwong, N. Yoshinari, T. Kojima, and T. Konno, *Chem. Commun.* **2016**, *52*, 12893-12896; (g) M. Kouno, N. Kuwamura, N. Yoshinari, and T. Konno, *Chem. Lett.* **2017**, *46*, 1542-1545; (h) N. Oya, M. Yamada, S. Surinwong, and N. Kuwamura, T. Konno, *Dalton. Trans.* **2018**, *47*, 2497-2500.
10   (a) R. Lee, A. Igashira-Kamiyama, M. Okumura, and T. Konno, *Bull. Chem. Soc. Jpn.* **2013**, *86*, 908-920; (b) N. Yoshinari, C. Li, R. Lee, N. Kuwamura, A. Igashira-Kamiyama, and T. Konno, *Inorg. Chem.* **2015**, *54*, 8881-8883; (c) M. Yamada, *et al.*, *Chem. Sci.*, **2017**, *8*, 2671-2676; (d) T. Itai, T. Kojima, T. Konno, *Bull. Chem. Soc. Jpn.* **2017**, *90*, 1273-1275; (e) T. Itai, T. Kojima, N. Kuwamura, and T. Konno, *Chem. Eur. J.* **2017**, *23*, 16438-16441.
11   (a) Y. Kurioka, N. Kuwamura, N. Yoshinari, A. Igashira-Kamiyama, and T. Konno, *Chem. Lett.* **2015**, *44*, 1330-1332; (b) N. Kuwamura, Y. Kurioka, and T. Konno, *Chem. Commun.* **2017**, *53*, 846-849.
12   K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 5th ed., Wiley, Chichester, **1997**.
13   CCDC 1849565, 1849566 and 1849567 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.
14   B.-C. Tzeng, W.-F. Fu, C.-M. Che, H.-Y. Chao, K.-K. Cheung, and S.-M. Peng, *J. Chem. Soc. Dalton Trans.* **1999**, 1017-1024.
15   Two water molecules contact with vacant coordination sites on each Cu^{II} atom ($Cu–O$ = 2.797 Å).
16   We have confirmed the stability of compounds in the course of the electrolysis, based on the absorption, CD, and X-ray photoelectron spectral measurements.
17   A. L. Gibb, N. Alem, J.-H. Chen, K. J. Erickson, J. Ciston, A. Gautam, M. Linck, and A, Zettl, *J. Am. Chem. Soc.* **2015**, *137*, 6758-6761.
18   (a) X. Sala, S. Maji, R. Bofill, J. García-Antón, L. Escriche, and A. Llobet, *Acc. Chem. Res.* **2014**, *47*, 504-516; (b) H.-H. Huang, J.-W. Wang, P. Sahoo, D.-C. Zhong, and T.-B. Lu, *Chem. Commun.* **2017**, *53*, 9324-9327.
19   It has been reported that a metal center with lower coordination number shows a higher catalytic activity: for example, (a) Y. Nishida, M. Takeuchi, N. Oishi, S. Kida, *Inorg. Chim. Acta* **1985**, *96*, 81-85; (b) M. J. Gajewska, W.-M. Ching, Y.-S. Wen, C.-H. Hung, *Dalton Trans.* **2014**, *43*, 14726-14736; (c) X.-Y. Li, L. Gao, Y. Zhang, S. F. Akogun, W.-K. Dong, *RSC. Adv.* **2017**, *7*, 35905-35916; (d) S. M. Brewer, K. R. Wilson, D. G. Jones, E. W. Reinheimer, S. J. Archibald, T. J Prior, M. A. Ayala, A. L. Foster, T. J. Hubin, K. N. Green, *Inorg. Chem.* **2018**, *57*, 8890-8902.