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Subtle Changes, Dramatic Effects: Homogeneous Catalysis of the Oxygen-Reduction Reaction

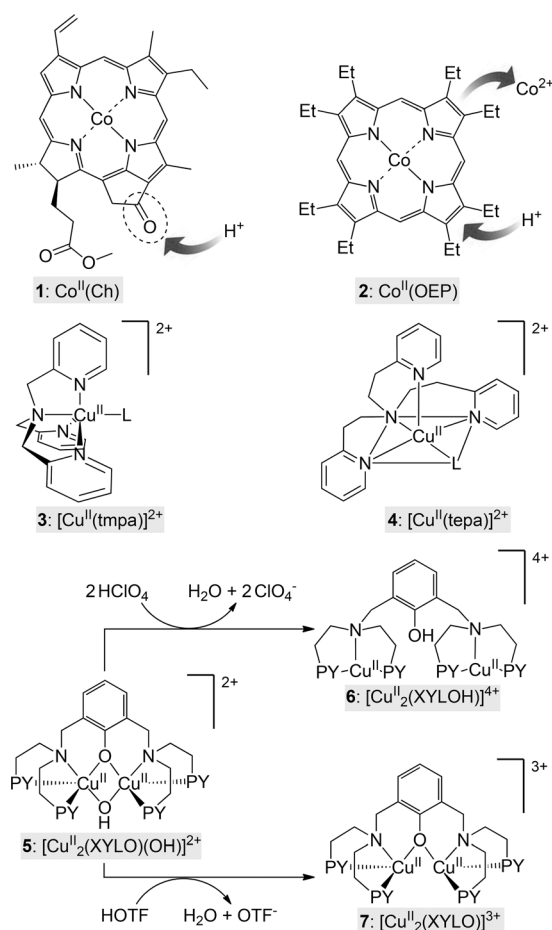
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The rigorous probing of the factors that underpin the mechanisms of the $2e^-/2H^+$ and $4e^-/4H^+$ catalytic oxygen-reduction reaction (ORR) pathways to afford H_2O_2 and water, respectively, by using non-precious-metal complexes, primarily of cobalt, copper, and iron, has facilitated breakthroughs in our understanding of fundamental biological processes and in the development of optimally designed catalysts for technological applications, such as in fuel cells.^[1] The electrochemical monitoring of heterogeneous ORRs by tethering a metal complex to a solid electrode surface limits access to mechanistic data by preventing detailed variable-solution-temperature kinetics and the spectroscopic monitoring of metal– O_2 intermediates.^[2] However, no such restrictions apply to homogeneous ORRs in non-aqueous media that contain a solubilized metal complex as a catalyst, an organic acid as a proton source, and a ferrocene (Fc)-derived one-electron reductant.^[2] The chemical-reduction approach allows the determination of the stoichiometry of the overall reaction, whilst separately focusing on key intermediate steps in the catalytic cycle.^[2]

Herein, we highlight the recent work of Fukuzumi and co-workers, who have made an art out of elucidating precise homogeneous catalytic ORR mechanisms and teasing out “cause and effect” relationships between subtle changes in the catalyst, that is, ligand design or reaction conditions, and the ensuing, often dramatic, experimentally observed mechanistic changes.

Dicobalt bisporphyrins efficiently catalyze the $4e^-/4H^+$ ORR, whereas monomeric cobalt porphyrins, phthalocyanines, and corroles act as selective $2e^-/2H^+$ ORR catalysts through Fc derivatives in non-aqueous media with an organic acid.^[3] Fukuzumi and co-workers report a new type of N4-macrocyclic Co complex, a cobalt chlorin ($[Co^{II}(Ch)]$, **1**; Scheme 1), and perform a direct comparison with a cobalt–porphyrinoid complex ($[Co^{II}(OEP)]$, **2**; Scheme 1), in which OEP^{2-} is the octaethylporphyrin dianion), with an emphasis on the enhanced acid stability and catalytic reactivity of complex **1** relative to complex **2** under identical experimental conditions.^[4]

Complex **2** deactivates in benzonitrile with perchloric acid ($HClO_4$) at 298 K, owing to demetalation through electrophilic H^+ attack on the core pyrrole N atoms to give $H_2(OEP)$, followed by further protonation to form $[H_4(OEP)]^{2+}$. No demeta-



Scheme 1. Copper- and cobalt-based complexes as catalysis for the homogeneous oxygen-reduction reaction (adapted from Refs [4, 7, and 8]).

lation was observed for complex **1**, which maintained robust catalysis with a turnover number $> 30\,000$. The relatively large core size and enhanced flexibility of the Ch ligand allowed easy incorporation of the low-valence Co ion. Crucially, the Ch ligand possesses a carbonyl group at the C13 position, in conjugation with the π system. Protonation of this carbonyl group to form the $[Co^{II}(ChH)]^+$ complex decreases the electron density on the Ch ligand. The nucleophilicity of the core pyrrole N atoms and, thus, their susceptibility towards electrophilic H^+ attack is decreased. Electrochemical measurements revealed that protonation of the ligand, thus forming a protonated Co^{III} intermediate, also shifts the onset potential for the catalytic $2e^-/2H^+$ ORR from 0.48 V versus SCE in benzonitrile (all further potentials reported herein are relative to SCE in the respective

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non-aqueous medium), in the absence of HClO_4 , to 0.37 V. Indeed, for a monomeric Co complex, this value is the smallest ORR overpotential reported so far and is again attributed to the decrease in electron density of the Ch ligand on protonation. This result is significant because tuning the overpotential for Co complexes requires fine balancing to obtain a Co^{III} intermediate with as positive a reduction potential as possible, to decrease the overpotential, but not so positive as to prevent the Co^{II} species from reacting with O_2 . Spectroscopic studies revealed that only complex **1** was catalytically active enough to reduce O_2 on replacing any of the stronger reductants with the weakest, that is, dibromoferrrocene (Br_2Fc).

Fukuzumi and co-workers have also turned their attention to Cu-based complexes and they have reported one dinuclear and two mononuclear Cu complexes that catalyze the homogeneous $4e^-/4\text{H}^+$ ORR, as well as one dinuclear Cu complex that catalyzes the homogeneous $2e^-/2\text{H}^+$ ORR.^[5,6] Each of these systems required a strong reductant, such as decamethylferrocene (Fc^*).^[5,6] Recently, they re-visited one of the mononuclear complexes that catalyzed the $4e^-/4\text{H}^+$ ORR, $[\text{Cu}^{\text{II}}(\text{tmpa})]^{2+}$ ($\text{tmpa} = \text{tris}(2\text{-pyridylmethyl})\text{amine}$),^[7] and the dinuclear Cu complex that catalyzed the $2e^-/2\text{H}^+$ ORR, $[\text{Cu}^{\text{II}}_2(\text{XYLO})(\text{OH})]^{2+}$ ($\text{XYLO} = m\text{-xylene-linked bis}[(2\text{-pyridyl})\text{ethyl}]\text{amine}$) dinucleating ligand with a Cu-bridging phenolate moiety).^[8] In their first study, a subtle change in ligand architecture was introduced, that is, the addition of one methylene group in the Cu^{II} -pyridylalkyl moiety of $[\text{Cu}^{\text{II}}(\text{tmpa})]^{2+}$ (**3**), thus forming $[\text{Cu}^{\text{II}}(\text{tepa})]^{2+}$ (**4**, $\text{tepa} = \text{tris}[2\text{-}(2\text{-pyridyl})\text{ethyl}]\text{amine}$; Scheme 1).^[7] In the second study, a modification of the reaction conditions was investigated, that is, the use of a stronger organic acid, HClO_4 , instead of trifluoroacetic acid (HOTF), with $[\text{Cu}^{\text{II}}_2(\text{XYLO})(\text{OH})]^{2+}$ (**5**, Scheme 1).^[8] With these Cu complexes, a non-coordinating solvent, that is, acetone, was essential because a coordinating solvent prohibited the chemistry discussed below.

The incorporation of an extra methyl group changed the coordination geometry of a solvent ligand (L) from trigonal-bipyramidal (with complex **3**) to square-based pyramidal (with complex **4**, Scheme 1).^[7] This shift from forming a five-membered chelate ring to a six-membered chelate ring with Cu^{II} and the ensuing larger ligand-binding constants to Cu^{II} elicited a large positive shift in the $\text{Cu}^{\text{II/I}}$ redox potential from -0.03 V for complex **3** to 0.44 V for complex **4**. Thus, electron transfer from relatively weak reductants, such as Fc ($[E_{\text{Fc}^+/\text{Fc}}^0]_{\text{SCE}}^{\text{acetone}} = 0.37$ V) or dimethylferrocene (Me_2Fc ; $[E_{\text{Me}_2\text{Fc}^+/\text{Me}_2\text{Fc}}^0]_{\text{SCE}}^{\text{acetone}} = 0.26$ V), to complex **4** occurred, thus forming $[\text{Cu}^{\text{I}}(\text{tepa})]^+$. Cu^{I} complexes with rather positive one-electron-oxidation potentials cannot typically bind O_2 and facilitate the crucial initial reduction step to the peroxide level. However, the presence of HClO_4 drives the reaction towards the formation of a Cu^{II} -hydroperoxo species, thereby producing the key $[\text{Cu}^{\text{II}}(\text{tepa})\text{OOH}]^+$ intermediate. The position of the hydroperoxo ligand in the coordination environment of $[\text{Cu}^{\text{II}}(\text{tepa})\text{OOH}]^+$ is different to that in the homologous $[\text{Cu}^{\text{II}}(\text{tmpa})\text{OOH}]^+$ complex. Moreover, it is likely that the Cu–O bond is comparatively elongated for $[\text{Cu}^{\text{II}}(\text{tepa})\text{OOH}]^+$. Either or both of these factors may be responsible for the

cleavage of the hydroperoxide group by acid, to preferably produce H_2O_2 with $[\text{Cu}^{\text{II}}(\text{tepa})\text{OOH}]^+$,^[7] whereas the $[\text{Cu}^{\text{II}}(\text{tmpa})\text{OOH}]^+$ intermediate released water.^[5] Surprisingly, the $2e^-/2\text{H}^+$ ORR with Me_2Fc and complex **4** exhibited no temperature dependence; however, a highly plausible explanation for this seemingly unusual finding was elucidated from detailed variable-solution-temperature kinetics investigations.^[7]

In the presence of HClO_4 , complex **5** undergoes protonation of both the hydroxide and phenoxo moieties to form $[\text{Cu}^{\text{II}}_2(\text{XYLOH})]^{4+}$ (**6**).^[8] However, in the presence of HOTF, only protonation of the hydroxide group occurs, thus forming $[\text{Cu}^{\text{II}}_2(\text{XYLO})]^{3+}$ (**7**, Scheme 1). Thus, for compound **6**, the phenoxo O atom no longer bridges the Cu^{II} ions, with each metal center now independent and electron deficient relative to complex **7** (in which the Cu^{II} ions remain bridged). Accordingly, the effective overpotential for the reduction of complex **6** into an O_2 -binding Cu^{I}_2 species or a mixed-valence $\text{Cu}^{\text{II}}\text{Cu}^{\text{I}}$ species drops by about 0.3 V to 0.47 V. Energetically, weak electron donors may now reduce complex **6**, but not complex **7**. The Cu^{II} -hydroperoxo species in this catalytic cycle, $[\text{Cu}^{\text{II}}_2(\text{XYLO})(\text{OOH})]^{2+}$, ultimately determines whether $2e^-/2\text{H}^+$ or $4e^-/4\text{H}^+$ O_2 reduction is observed. HOTF readily protonates the hydroperoxo ligand, thus giving H_2O_2 ; however, unlike HClO_4 , it is not strong enough to allow proton-coupled electron transfer (PCET) hydroperoxide reduction into water.

These recent advances by Fukuzumi and co-workers, which constitute 1) the first reports of selective $2e^-/2\text{H}^+$ and $4e^-/4\text{H}^+$ oxygen-reduction reactions with mononuclear and dinuclear Cu-based complexes, respectively, at low enough overpotentials to use less-potent one-electron reductants than Fc^* and 2) a highly active and stable Co–chlorin catalyst with the smallest ORR overpotential reported thus far for a monomeric Co complex, deserve to be highlighted because they provide fundamental mechanistic clues that may ultimately lead to the development of optimal catalysts for fuel cells.^[9]

Keywords: cobalt · copper · electron transfer · homogeneous catalysis · reduction

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