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Controlled O₂ reduction at a mixed-valent (II,I) Cu₂S core.

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Inspection of Oxygen Reduction Reactions (ORR) using a mixed-valent Cu₂S complex as pre-catalyst revealed a tuneable H₂O₂ vs. H₂O production under mild conditions by controlling the amount of sacrificial reducer. The fully reduced bisCuI state is the main active species in solution, with fast kinetics. This new catalytic system is robust for H₂O₂ production with several cycles achieved and opens up perspectives for integration into devices.

With the increase in world population and the shrinking of unsustainable fossil fuels that we depend on, there is a crucial need in exploring carbon-free alternatives to ensure a safe and sustainable future. In this line, the so-called Oxygen Reduction Reactions (ORR) are important processes in fuel cells technology[1] for achieving a hydrogen-based society.[2] However this cathodic event remains the limiting step regarding the efficiency of a complete device.[3] ORR find its essence in Nature with biological respiration[4] including laccases that catalyse the 4e-/4H₊ reduction of O₂ into H₂O.[5] The other important product formed upon O₂ reduction is hydrogen peroxide (H₂O₂) via a 2e-/2H₊ process. H₂O₂ is important for living organisms where it is for instance biosynthesized by the immune system to kill microbes,[6] as signal molecule under oxidative stress conditions[7] or used for metabolic purposes by copper metalloenzymes such as Galactose Oxidase.[5b] It is a staple in the industry with a ranking in the top 100 most important reactants with more than 3 million tons produced per year[8] and widely used in pharmaceuticals, cosmetics and electronics.[9] H₂O₂ has recently emerged as a potent latent energy carrier through its O-O bond (Gibbs free energy of formation of $\Delta G_f^0 = -120 \text{ kJ mol}^{-1}$ from H₂ and O₂) and is thus a suitable candidate for energy storage for fuel cells technology.[10] However, given a production that mainly relies on the energy-consuming and precarious anthraquinone process,[11] new eco-friendly methodologies for controlled H₂O₂ production from O₂ reduction have yet to be discovered.

The conception of efficient catalysts for homogeneous ORR based on noble but also non-noble metal ions such as Fe, Co or Mn has stimulated intensive research.[12] In these cases, the electron source for the catalytic activity comes from sacrificial reducers such as metallocenes or via electrocatalysis. With respect to homogenous Cu-based catalysts, mono-, [13] di- [14] and trinuclear [15] copper complexes have been studied and relevant activities reported. Interestingly, the presence of Lewis acid (Sc³⁺) was shown to induce selective catalysis towards two-electron O₂ reduction.[16] Under heterogeneous conditions, immobilized Cu complexes are particularly efficient for O₂ reduction into H₂O.[17]

With the aim of targeting ORR with original dicopper systems, we report here the activity of our previously described mixed-valent (MV) copper complex 1 [18] possessing a N₆Cu₂S environment (Figure 1). We evidenced a tuneable chemical H₂O₂ vs. H₂O selectivity in acetonitrile using controlled amounts of ferrocene derivatives as electron sources and in the presence of an organic acid. This

study represents, to the best of our knowledge, the first example for selective ORR involving a Cu₂S core under homogeneous and mild conditions.

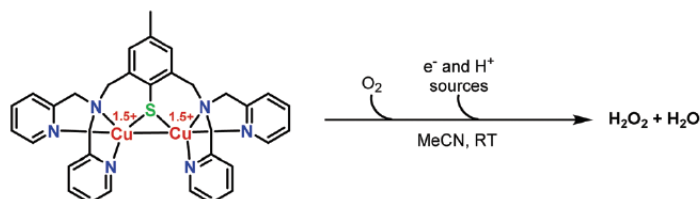


Fig. 1 Chemical structure of **1** and targeted ORRs.

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Catalytic ORR by **1** (0.05 mM, final concentration) were evaluated at room temperature (298 K) in air-saturated MeCN solutions. 2,6-lutidinium tetrafluoroborate (LutHBF₄, 400 molar equiv.) was used as innocent proton donor (weak coordinating ability of both the conjugate base and the BF₄-counter-anion) and sacrificial electrons (10 to 100 molar equiv.) were provided by the means of ferrocene (Fc, $E_{1/2} \text{Fc}^{+/0} = 0 \text{ V vs. Fc}^{+/0}$), dimethylferrocene (Me₂Fc, $E_{1/2} \text{Me}_2\text{Fc}^{+/0} = -0.10 \text{ V vs. Fc}^{+/0}$), octamethylferrocene (Me₈Fc, $E_{1/2} \text{Me}_8\text{Fc}^{+/0} = -0.42 \text{ V vs. Fc}^{+/0}$) or decamethylferrocene (Me₁₀Fc, $E_{1/2} \text{Me}_{10}\text{Fc}^{+/0} = -0.49 \text{ V vs. Fc}^{+/0}$). Fc and Me₂Fc are not compatible with the in situ reduction of any redox form of **1** ($E_{1/2}^{\text{I}} = -0.44 \text{ V vs. Fc}^{+/0}$, $\Delta E = 0.07 \text{ V}$, Cu₂I,II → Cu₂I,I; $E_{1/2}^{\text{II}} = -0.30 \text{ V vs. Fc}^{+/0}$, $\Delta E = 0.08 \text{ V}$, Cu₂I,II → Cu₂II,II),[18] whereas Me₈Fc and Me₁₀Fc are suitable for these processes. Monitoring the reaction by UV-Visible (UV-vis) spectrophotometry unambiguously shows the formation of Fc⁺, Me₂Fc⁺, Me₈Fc⁺ or Me₁₀Fc⁺ at 614 nm ($\epsilon = 410 \text{ M}^{-1} \text{ cm}^{-1}$), 650 nm ($\epsilon = 290 \text{ M}^{-1} \text{ cm}^{-1}$), 750 nm ($\epsilon = 390 \text{ M}^{-1} \text{ cm}^{-1}$) and 778 nm ($\epsilon = 495 \text{ M}^{-1} \text{ cm}^{-1}$), respectively (Figs. S1-S8 and Table S1, ESI) and attests for O₂ reduction in all cases. Interestingly, only 2 molar eq. of Fc⁺ and 30 molar eq. of Me₂Fc⁺ (Figs. S3 and S4) are detected when going up to 100 molar eq., whereas the maximum of possible turnover numbers (TONs) is reached with Me₈Fc and Me₁₀Fc (denoted Me8-10Fc when compared in the following) regardless the excess (Fig. 2 and Figs S5-S8, ESI).

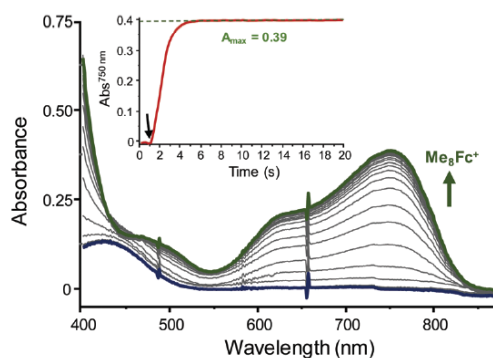


Fig. 2 Representatives UV-vis spectra for Me₈Fc⁺ accumulation during ORR mediated by **1** in air-saturated MeCN at 298 K using **1**/Me₈Fc/LutHBF₄ at 1/20/400; inset: variation of the Abs_{750nm} as a function of time (the green dotted line indicates the theoretical A_{max} for total Me₈Fc conversion); the black arrow indicates the injection of **1**.

Quantitative Me₈-10Fc⁺ formation allowed the use of the H₂O₂-specific TiO-tpyp procedure (Fig. S9, ESI) in order to discriminate between H₂O₂ and H₂O production.[19] This method is extremely precise compared to iodine titration. H₂O production was calculated considering the amount of Me₈-10Fc⁺ not involved in H₂O₂ formation (see ESI for more details).

A key result is the change in selectivity, H_2O_2 vs. H_2O , obtained by varying the amount of $\text{Me}_{8-10}\text{Fc}$ (Table 1): almost exclusive H_2O_2 formation occurs with 10 molar eq., whereas going to 100 molar eq. mainly leads to H_2O production (entries 1 and 6, Table 1). The selectivity is moderately affected by either the kinetics or the difference in the reducing abilities of $\text{Me}_{8-10}\text{Fc}$ ($\Delta E_{1/2} = 0.07$ V). As control experiments, no O_2 or H_2O_2 reduction by $\text{Me}_{8-10}\text{Fc}$ occur under the same conditions (and reaction times) in the absence of **1** (Fig. S10, ESI). This strongly supports a H_2O formation process originating from a catalysed two-electron reduction of a coordinated (hydro)peroxide at high $\text{Me}_{8-10}\text{Fc}$ concentrations. The inactivity of low-valent $[\text{Cu}(\text{Tol})_2](\text{OTf})$ ($\text{OTf} =$ trifluoromethanesulfonate anion and $\text{Tol} =$ toluene) finally reinforces the remarkable effect of the S/N coordination spheres in **1** on the reactivity and excludes solvated CuI ions as activators.

Kinetically speaking, the fact that the reactions with Fc and Me_2Fc are relatively slow and not complete compared to those with $\text{Me}_{8-10}\text{Fc}$ (Table 1 and Table S2, ESI) suggests that **1** or its protonated form $\mathbf{1}^{\text{H}}$ (see below for the behaviour of **1** with LutHBF_4) could initiate the reaction. However, its rather modest efficiency indicates that MV states cannot be considered as the most active forms. It also demonstrates that the redox potentials of the oxidized species generated along the reaction course are not (or partially) thermodynamically compatible with the reducing abilities of Fc and Me_2Fc to reach total consumption of the electron source.

Consequently, from now on, only the case of $\text{Me}_{8-10}\text{Fc}$ is discussed since quantitative and fast conversions were obtained. For 10 and 20 molar eq., the kinetic traces (Figs. S5 and S7, ESI) display pseudo-first-order profiles and comparable reaction times. Starting with 40 molar eq. and above, the reaction times are significantly shorter with Me_{10}Fc compared to Me_8Fc , for which successive steps are identifiable (Figs. S5-S8, ESI). The overall comparison of the kinetics traces clearly indicates the involvement of more active species when using Me_{10}Fc compared to Me_8Fc . It is worth noting that the kobs values are inversely proportional or quasi-independent with respect to $[\text{Me}_8\text{Fc}]$ (to a certain extent) or $[\text{Me}_{10}\text{Fc}]$, respectively (Fig. S11, ESI). This suggests that the gradual accumulation of H_2O results in competitive reaction pathways for Me_8Fc (with a global steady state starting from 60 molar eq.) that are not present for Me_{10}Fc (its consumption not being the rate-determining step).

This new catalytic system has proven to be robust for H_2O_2 production, especially in the most favourable conditions. For instance, at least four consecutive cycles were achieved with successive additions of 10 molar eq. Me_8Fc and its quantitative consumption after each injection (Fig. S12). An overall selectivity of 85% in H_2O_2 , similar to that observed for a single run, was determined. This result demonstrates that H_2O_2 accumulation neither (i) affects the selectivity/efficiency nor (ii) poisons the catalyst.

The behaviour of **1** in the presence of $\text{Me}_{8-10}\text{Fc}$ and LutHBF_4 prior exposure to air was then investigated in order to get insights into the nature of putative relevant copper species involved during the O_2 reduction process. For solubility reasons, as the concentrations required to perform such experiments are different from those used for catalysis, only one condition (i.e. 10 molar eq. $\text{Me}_{8-10}\text{Fc}$ and 400 molar eq. LutBF_4) was tested. Since identical results were obtained whatever the nature of the electron source, only the data obtained with Me_8Fc are discussed. Under strict anaerobic conditions, the UV-vis/NIR spectrum of **1** is modified upon addition of LutHBF_4 and / or Me_8Fc (Fig. S13, ESI). The presence of protons leads to the formation of a new $\mathbf{1H}$ species with conservation of a dinuclear delocalized MV state (absorbance in the NIR region).

Table 1. ORR experiments performed with **1** at room temperature using Me₈₋₁₀Fc and LutHBF₄ as electron and proton sources. ^(a)

Table 1 ORR experiments performed with **1** at room temperature using Me₈₋₁₀Fc and LutHBF₄ as electron and proton sources^a

Entry	[Me ₈₋₁₀ Fc] (mM)	Cat/e ⁻ /H ⁺	% H ₂ O ₂ Me ₈ Fc/ Me ₁₀ Fc	% H ₂ O Me ₈ Fc/ Me ₁₀ Fc	TON	TON _{max}	k _{obs} (s ⁻¹) Me ₈ Fc/Me ₁₀ Fc	t (s) Me ₈ Fc/Me ₁₀ Fc
1	0.5	1/10/400	90/82	10/18	10	10	1.06 ± 0.02/0.47 ± 0.02	4.1 ± 0.2/5.6 ± 0.3
2	1.0	1/20/400	83/72	17/28	20	20	0.61 ± 0.02/0.39 ± 0.02	6.5 ± 0.3/5.9 ± 0.3
3	2.0	1/40/400	57/58	43/42	40	40	0.28 ± 0.04/0.52 ± 0.03	15.0 ± 0.4/6.0 ± 0.5
4	3.0	1/60/400	51/37	49/63	60	60	0.13 ± 0.01/0.62 ± 0.04	28.1 ± 0.5/5.9 ± 0.3
5	4.0	1/80/400	38/10	62/90	80	80	0.15 ± 0.01/0.60 ± 0.03	32.1 ± 1/6.2 ± 0.3
6	5.0	1/100/400	10/5	90/95	100	100	0.12 ± 0.01/0.41 ± 0.02	41.2 ± 2/10.6 ± 0.4

^(a) See the ESI for further experimental details.

As expected, Me₈Fc in excess can reduce **1** to form **1**_{red}. Addition of both the electron and proton sources results in the formation Me₈Fc⁺, the loss of the MV signature of **1** and the generation of the reduced/protonated form **1**_{red}^H. In this case, the spectrum of the final mixture can be adjusted by combining 10% of remaining **1**^H, 0.9 molar eq. Me₈Fc⁺ and 9.1 molar eq. Me₈Fc. **1**_{red}^H should weakly contribute to the final spectrum due to the presence of d¹⁰ Cu^I ions. In the meantime, the EPR spectra show modifications of the hyperfine when **1** is converted into **1**^H, followed by the decrease of the signal intensity consecutive to the reduction into **1**_{red}H (10% remaining intensity, Fig. S14, ESI). An identical spectrum was obtained by adding a mixture of protons and electrons to a solution of **1**. Finally, the low-valent state was trapped by ESI-MS using similar experimental conditions (Fig. S15, ESI). All these experiments provide solid evidences for a mono-electronic reduction/protonation process of **1** into **1**_{red}^H via **1**^H. Independently, exposition of a solution of **1**_{red}H to air lead to full Me₈Fc consumption and the H₂O₂/H₂O ratio is in line with that reported in Table 1 (entry 1). These results clearly indicate that low-valent **1**_{red}H is highly reactive and a key actor during catalysis.

O₂ oxidation of **1** has also to be considered as part of the catalytic event. The corresponding **1**_{ox} form was generated by exposing a MeCN solution of **1** to air. Its crystal structure shows the presence of a doubled-bridged dicopper(II) unit involving the S atom from the ligand and an additional hydroxyl anion (Fig. S16, ESI). **1**_{ox} has a significantly different UV-vis/NIR spectrum compared to its precursor with the loss of the NIR band (Fig. S17, ESI). The extinction of the EPR signal (> 90%, Fig. S18, ESI) agrees with a strong antiferromagnetic coupling between the two metal ions leading to a S = 0 ground state. Such magnetic behaviour was already observed with a similar scaffold[20] or in the case of a phenolate spacer with identical Me(N,N-bis(methylpyridyl))amine pendant arms.[21] The ESI-MS spectrum of **1**_{ox} (Fig. S19, ESI) shows two prominent peaks at m/z = 344.3 (Δm/z = 0.5) and 839.3 (Δm/z = 1.0) consistent with the solved solid-state structure. Catalytic experiments with **1**_{ox}, 10 molar eq. Me₈Fc and 400 molar eq. LutHBF₄ lead to quantitative conversion within a reaction time scale close to that of **1** (k_{obs} = 1.17 s⁻¹, Fig. S20 in ESI). H₂O₂ titration indicates a selectivity similar to that of **1** (88/12 for H₂O₂/H₂O). The activity of **1**_{ox} is in line with its facile protonation (to **1**_{ox}^H) and reduction (Fig. S21, ESI) under anaerobic conditions. Such species could thus be part of the reactivity.

These results suggest that the H₂O₂/H₂O production cycle mainly relies on **1**_{red}^H and allow the proposition of a reaction scheme (Scheme 1). **1**_{red}H is generated by reduction/protonation of **1** or alternatively by air oxidation/protonation/reduction of **1** via **1**_{ox}^H (Fig. S22, ESI). O₂ activation at **1**_{red}H followed by protonation lead to the key

O₂-adduct(s) from which the selectivity can be explained by the inevitable competition between its protonation and/or reduction. Taking into account the composition of the mixture at the end of the reaction (presence of O₂, LutHBF₄ and Me₈Fc⁺), **1**_{ox}H is certainly the final fate of the catalyst, as

observed by ESI-MS (Fig. S23, ESI). This proposition is also reinforced by the ability of performing several cycles, necessarily through an oxidized species, with no loss in selectivity and efficiency. Nevertheless, 1oxH cannot be considered as a predominantly active species during catalysis at that point, since H₂O would be the main product under any experimental condition.

To conclude, we demonstrate here that copper/sulphur assemblies such as 1 are very efficient for ORR at room temperature with fast kinetics. By controlling the amount of Me₈₋₁₀Fc, a significant and tuneable H₂O₂ vs. H₂O selectivity can be achieved. H₂O accumulation results from peroxide ligation and reduction at an active species since H₂O₂ is not reduced in situ in the absence of 1. The reductive power of the reaction mixture is a factor that helps explaining the selectivity. With rather “low excess” Me₈₋₁₀Fc, the two-electron reduction into H₂O₂ is favoured. When the concentration of the electron source increases, a competition between H₂O₂ release and its subsequent reduction sets up and becomes gradually predominant. Independently, a similar study with 1ox will be of great interest to compare its reactivity with a related phenolate-bridged dicopper II complex, whose ability for ORR was reported in 2012.[14c] The impact of the thiophenolate vs phenolate moiety could be appreciated (at first approximations 1ox seems faster) and correlated to electronic properties. In a different light, even if H₂O₂ is quite an aggressive molecule in solution, the observation that several cycles can be performed with successive Me8Fc injections attests for the robustness of the system. These results are encouraging for further applications in heterogeneous catalysis upon grafting air stable 1ox whether onto an inert surface with the presence of an external electron source or on electroactive materials for electrocatalysis. Finally, a global reaction sequence for the activity of 1 and its derivatives is proposed and is now under dissection with complementary kinetic experiments and the characterization of the pivotal O₂-adduct(s).

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Conflicts of interest

There are no conflicts to declare.

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