Electronic Supplementary Information

for

O-O bond cleavage by electrochemical reduction of a side-on peroxo dicopper model of hemocyanin.

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1. Experimental and methods

The syntheses of the complexes $\text{1}^{2+}$ [Cu$_2$(H6M4h)(CH$_3$CN)]$^{2+}$ and [Cu$_{10}$(H6M4h)(µ-OH)$_2$]$^{2+}$ were previously described.$^{1,2}$ Room temperature electrochemical studies of the copper complexes were performed in a glovebox (Jacomex) ($\text{O}_2 < 1$ ppm, $\text{H}_2\text{O} < 1$ ppm) with a home-designed 3-electrodes cell (WE: glassy carbon or platinum, RE: Pt wire in a $\text{Fc}^+$/Fc solution, CE: Pt or graphite rod). Ferrocene was added at the end of the experiments to determine redox potential values. The potential of the cell was controlled by an AUTOLAB PGSTAT 100 (Metrohm) potentiostat monitored by the NOVA 1.11 software. “Extra-dry” dichloromethane stabilized on molecular sieves was purchased from Acros. The supporting salt NBu$_4$PF$_6$ was synthesized from NBu$_4$OH (Acros) and HPF$_6$ (Aldrich). It was then purified, dried under vacuum for 48 hours at 100° C, then kept under argon in the glovebox. Thin layer UV-Vis spectroelectrochemistry was performed with a specific home-designed cell in a reflectance mode (WE: GC, RE: Pt wire, CE: Pt wire). The UV-Vis optic fibre probes were purchased from Ocean Optics. Time-resolved UV-Vis detection was performed with a QEPro spectrometer (Ocean optics, minimum response time 8 ms). EPR spectra were recorded on a Bruker ELEXSYS apparatus (X-band, $\nu=9.35$ GHz) at low temperature ($T =130$ K). EPR simulation was performed with the XSophe software (Bruker).

2. Figures

![Figure S1. Rotating-disk voltammograms at a vitreous carbon electrode of $\text{1}^{2+}$ in CH$_2$Cl$_2$/NBu$_4$PF$_6$ under argon A) before electrolysis at different rotating speed ($\omega$); insert: $i_{\text{lim}}$ vs $\omega^{1/2}$.B) a) before and b) after electrolysis at $E = 0.90$ V ($\omega = 1000$ t.min$^{-1}$).](image)
Figure S2. Cyclic voltammograms at a vitreous carbon electrode of $2^{+}$ in CH$_2$Cl$_2$/NBu$_4$PF$_6$ under argon (obtained by electrolysis of $1^{2+}$ at $E = 1.0$ V) ($0.02 < \nu < 2$ V.s$^{-1}$). Insert: plots of $i_{pc}$ (2) vs $\nu^{1/2}$. B) a) experimental and b) simulated EPR spectra of the electro-generated bis-Cu(II) complex at 150 K.

Figure S3. UV-Vis spectrum of $2^{+}$ in CH$_2$Cl$_2$/NBu$_4$PF$_6$ under argon (obtained by electrolysis of $1^{2+}$ at $E = 1.0$ V).
Figure S4. Evolution of A) UV-Vis spectra and B) Cyclic voltammograms at vitreous carbon electrode of $1^{2+}$ in CH$_2$Cl$_2$/NBu$_4$PF$_6$ under argon at $v = 0.1$ V/s after addition of O$_2$.

Figure S5. A) Rotating-disk electrode ($\omega = 1000$ t.min$^{-1}$) and B) Cyclic voltammograms ($v = 0.1$ V.s$^{-1}$) at a vitreous carbon electrode of $1^{2+}$ in CH$_2$Cl$_2$/NBu$_4$PF$_6$ under argon after addition of O$_2$. *: cathodic peak corresponding to O$_2$ reduction on vitreous carbon at $E = -1.45$ V.
**Figure S6.** A) Cyclic voltammograms \((0.02 < v < 1 \text{ V.s}^{-1})\) at a vitreous carbon electrode before electrolysis of \(3^{2+}\) in \(\text{CH}_2\text{Cl}_2/\text{NBu}_4\text{PF}_6\) at \(E = -0.90 \text{ V vs Fc}\). B) Plots of \(i_{pc}(3)\) vs \(v^{1/2}\). V) Plots of \(E_{pc}(3)\) vs \(\log v\).

**Figure S7.** CV at \(v = 0.1 \text{ V s}^{-1}\) of a solution of \(3^{2+}\) in 0.1 M \(\text{NBu}_4\text{PF}_6/\text{CH}_2\text{Cl}_2\) after exhaustive electrolysis at \(-1.0 \text{ V vs. Fc}\).
Figure S8. A) EPR (T=130 K, ν =9.35 GHz) spectrum of the electrolyzed (at -1.0 V) product of 3²⁺ (1 mM) (black curve) compared with that obtained for the mononuclear complex [Cu²⁺(TMPA)(H₂O)]²⁺ in the same experimental conditions (1 mM, CH₂Cl₂/NBu₄PF₆) (red curve) (TMPA=tris(pyridylmethyl)amine); B) EPR spectrum of the electrolyzed product of 3²⁺ in a lower intensity scale.

Figure S9. A) UV-vis spectrum of a solution of 3²⁺ in 0.1 M NBu₄PF₆/CH₂Cl₂ after exhaustive electrolysis at -1.0 V vs. Fc. B) A close view of the 500 – 850 nm region showing the presence of a d-d band.
Figure S10. UV-vis spectrum of $2^{4+}$ (black curve) and the reduced form of $3^{2+}$ obtained by electrolysis at -1.0 V vs. Fc (red curve) in 0.1 M $\text{NBu}_4\text{PF}_6/\text{CH}_2\text{Cl}_2$. B) A close view of the 500 – 100 nm region comparing the d-d band for the complexes.

Figure S11. A) UV-Vis spectrum and B) cyclic voltammograms (0.02 < $v$ < 2 V.s$^{-1}$) of $[\text{Cu}^{II}_2(\text{H6M4h})(\mu-\text{OH})_2]^{2+}$ in $\text{CH}_2\text{Cl}_2/\text{NBu}_4\text{PF}_6$. 

3. Estimation of the threshold pKa value for HAT from weak C-H bond (BDE = 80 kcal mol\(^{-1}\))

The threshold pK\(_a\) value was calculated on the basis of the next thermochemical square scheme:\(^3\)

\[
\begin{align*}
\begin{array}{c}
3^{2+} \xrightleftharpoons[pK_{a1}] \ [3-H]^{3+} \\
E_1^0 & \downarrow \text{BDE} \downarrow E_2^0 \\
3^+ \xrightleftharpoons[pK_{a2}] \ [3-H]^{2+} 
\end{array}
\end{align*}
\]

where electron transfer processes are coloured in blue and proton transfers in red.

The enthalpy of the [3-H]\(^{2+}\) bond (BDE) can thus be evaluated through \(E_1^0\) and pK\(_{a2}\) using equation\(^4\)

\[
\text{BDE} = 1.37pK_{a2} + 23.06 E_1^0 + C
\]

where C = 66 kcal mol\(^{-1}\).\(^5\)

On the other hand, a hydrogen atom transfer (HAT) from the C-H bond of an organic substrate to 3\(^{2+}\) will be favoured if BDE(C-H) ≤ BDE([3-H]\(^{2+}\)). Therefore, the threshold pK\(_a\) value for the HAT from a relatively weak C-H bond (BDE(C-H) = 80 kcal mol\(^{-1}\)) to 3\(^{2+}\) can be tentatively assessed taking \(E_1^0 = E_{pc}(3)\). However, it should be noted that the unknown exact value of \(E_1^0\) limits a full quantitative evaluation of the strength of 3\(^{2+}\) as a HAT reagent. Additionally, caution should be exercised when discussing HAT processes in terms of BDEs, since entropic terms can have a strong effect on the reactivity.

4. References