Acid/base triggered interconversion of $\mu-\eta^2: \eta^2$-peroxido and bis($\mu$-oxido) dicopper intermediates capped by proton-responsive ligands†

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Cu$_2$($\mu-\eta^2: \eta^2$-peroxido) and Cu$_2$($\mu$-oxido)$_2$ cores represent key intermediates in copper/dioxygen chemistry, and they are mechanistically important for biological hydroxylation and oxidation reactions mediated by dinuclear (type III) copper metalloenzymes. While the exact nature of the active species in different enzymes is still under debate, shifting equilibria between Cu$_x$/O$_2$ species is increasingly recognized as a means of switching between distinct reactivity patterns of these intermediates. Herein we report comprehensive spectroscopic, crystallographic and computational analysis of a family of synthetic Cu$_2$($\mu-\eta^2: \eta^2$-peroxido) and Cu$_2$($\mu$-oxido)$_2$ dicopper complexes with a bis(oxazoline) (BOX) capping ligand. In particular, we demonstrate that a reversible peroxido/bis(oxido) interconversion of the [Cu$_2$O$_2$] core can be triggered by peripheral (de)protonation events on the ligand backbone. As the copper ions in the enzymes are typically supported by histidine imidazoles that offer a backside N atom amenable to potential (de)protonation, it is well conceivable that the shifting of equilibria between the [Cu$_2$O$_2$] species in response to changes in local pH is biologically relevant.

A variety of Cu$_x$/O$_2$ intermediates with different dioxygen binding modes have been uncovered and their diagnostic spectroscopic features and distinct reactivities are reasonably well understood.1–3,6,7,11 Binuclear complexes with a $\mu-\eta^2: \eta^2$-peroxido dicopper[II] core (P in Scheme 1), as found in oxyhaemocyanin or oxy-tyrosinase, are among the most prominent species, and synthetically useful biomimetic analogs capable of hydroxylating exogenous phenol substrates are starting to emerge.11–14 In model studies, it has been shown that dicopper complexes bearing a bis($\mu$-oxido) dicopper[II] core (O) are capable of C–H bond hydroxylation as well.15–19 In solution, the thermodynamic preference for the P or the O core depends on

Introduction

Dioxygen binding to copper in the active sites of metalloenzymes has received much attention in past decades.1 These metalloenzymes serve as prototypes for the development of bioinspired catalysts that can mediate the selective oxidation and oxygenation of C–H bonds, which is increasingly relevant for viable fuel and chemical feedstock formation.2 Major research efforts in bioinorganic chemistry have been devoted to the development of small model complexes that mimic various aspects of the structure and function of the natural enzymes.3–6 Owing to their specific design, it is often possible to trap key intermediates in such systems and to characterize their intrinsic reactivities in much greater detail than for the metalloenzymes themselves. The ultimate challenge is to understand the origin of the remarkable selectivity of the biochemical role models and to exploit the same concepts for the development of efficient synthetic catalysts.2,6

Scheme 1 P and O isomers found to be in equilibrium with each other (A). Bis-oxazoline(BOX) ligands used in this work (B).
the subtle influence of the particular supporting ligand, the solvent and the nature of counterions, and in some cases both isomers have been reported to coexist in rapid equilibrium.\textsuperscript{13,19–22} These findings have spurred vivid discussions regarding the nature of the active species in hydroxylation reactions\textsuperscript{1,2,3,3–28} and the P/O core interconversion is increasingly recognized as being mechanistically relevant. Herein we report on an unprecedented pH-dependent P/O interconversion reaction, triggered by (de)protonation events in a bioinorganic model complex, which appears to be of particular relevance for such reactions in biological systems.

Results and discussion

We have recently shown that bidentate bis(oxazoline)s (BOXs), which are easily accessible and represent a privileged ligand class, are well-suited for supporting biomimetic Cu/O\textsubscript{2} chemistry.\textsuperscript{29} By spectroscopic means we demonstrated that several ligands, \textsuperscript{R,R}BOXs (Scheme 1B), reversibly bind to dioxygen to form \textsuperscript{\(\mu\)}\textsuperscript{\(\eta^2\)}\textsuperscript{\(\eta^1\)}-peroxodicopper(II) complexes, both in solution and in the solid state; the thermodynamic and kinetic parameters of the P core formation have been determined.\textsuperscript{29} Furthermore, we have shown that certain free bis(oxazoline)s, \textsuperscript{R,H}BOXs, exist as an equilibrium mixture between the diimine and imine-enamine tautomers.\textsuperscript{30} The latter are reminiscent of \(\beta\)-diketimines used extensively as anionic ligands after deprotonation, which led us to consider \textsuperscript{R,H}BOXs as proton responsive ligands.

We have now exploited this concept in bioinspired Cu/O\textsubscript{2} chemistry to study an acid/base triggered interconversion between an acid/base triggered interconversion reaction, triggered by (de)protonation events in a bioinorganic model complex, which appears to be of particular relevance for such reactions in biological systems.

Reactions of \textsuperscript{R,R}BOX with [Cu(MeCN)\textsubscript{4}]ClO\textsubscript{4} in tetrahydrofuran (THF) gave the air sensitive copper(I) complexes [\textsuperscript{R,R}BOX Cu(MeCN)\textsubscript{4}]ClO\textsubscript{4}, \(1 (R = R' = Me), 2 (R = Me, R' = H), 3 (R = R' = H)\) as colourless compounds (see ESI†). Oxygenation of \(1, 2\) and \(3\) in THF at 193 K led to deep purple coloured solutions of [\textsuperscript{R,R}BOX(THF)Cu](\(\mu\textsuperscript{-}\textsuperscript{\(\eta^2\)}\textsuperscript{\(\eta^1\)}O\textsubscript{2})ClO\textsubscript{4}, \(4 (R = R' = Me), P5 (R = Me, R' = H)\) and \(P6 (R = R' = H)\) with intense optical features around 330 nm (\(\varepsilon = 20 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}\)) and 500 nm (\(\varepsilon = 1 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}\)). For a detailed assignment we performed time-dependent density functional theory (TD-DFT) calculations on the \(\mu\textsuperscript{-}\textsuperscript{\(\eta^2\)}\textsuperscript{\(\eta^1\)} peroxido complex \(P5\), including a coordinating ClO\textsubscript{4}– anion in the simulations.\textsuperscript{31} In good agreement with experiment, the simulated spectrum for \(P5\) shows an intense absorption at 340 nm and a shallow band around 535 nm (Fig. 1b, see ESI† for a detailed discussion). The former absorption originates from a \(\sigma \rightarrow \sigma^*\) intra-core charge transfer (i.e., from an occupied in-plane \(d_{xy}(\text{Cu}^I)/\pi^*(\text{O}_2^2)/d_{xy}(\text{Cu}^II)\) bonding orbital combination into its antibonding counterpart), typically observed for \(\mu\textsuperscript{-}\textsuperscript{\(\eta^2\)}\textsuperscript{\(\eta^1\)} peroxido complexes.\textsuperscript{26,29,32} The shallow absorption band at 535 nm is assigned to an intra-core \(\pi^* \rightarrow \sigma^*\) transition (i.e., from the out-of-plane \(\pi^*\) of the O\textsubscript{2}– ligand into the in-plane \(d_{xy}(\text{Cu}^I)/\pi^*(\text{O}_2^2)/d_{xy}(\text{Cu}^II)\) antibonding orbital combination).

Single crystals of \(P4\) and \(P5\) were grown by Et\textsubscript{2}O diffusion into THF : acetone (1 : 1) solutions at 193 K. X-ray diffraction analysis revealed the centrosymmetric molecular structures of the dications (\(P4\) and \(P5\)) as shown in Fig. S11† and Fig. 2. Each copper ion is found in a slightly distorted square pyramidal (SP) coordination environment (\(\tau = 0.16\) in \(P4\), 0.14 in \(P5\)) consisting of the respective BOX capping ligand, the bridging side-on \(\mu\textsuperscript{-}\textsuperscript{\(\eta^2\)}\textsuperscript{\(\eta^1\)} peroxide (\(d_{\text{Cu-O}} = 1.92–1.93\) Å) and a THF solvent molecule bound in the apical position (\(d_{\text{THF-Cu}} = 2.32/2.33\) Å).
While the Cu···Cu separations of 3.52 Å (P4) or 3.50 av. Å (P5) are typical for P cores, the bridging peroxido ligands exhibit the largest bond lengths (P4: 1.56 Å, P5: 1.58 Å) reported so far for synthetic and biological Cu(μ-η²:η²-O₂)Cu systems (Table S3† presents a compilation of geometric and spectroscopic features of all literature-known μ-η²:η²-peroxidodicopper(II) species).15-28 Most of the metric parameters of P4 and P5 are in excellent agreement with those derived from Cu K-edge extended X-ray absorption fine structure (EXAFS) data, for the corresponding P cores obtained with the capping ligands (P4-HBOX (P4-HP) and H1-HBOX (H1-HP)).

Resonance Raman (rR) spectroscopy (λex = 633 nm) of a THF solution of P4 at 193 K (Fig. 3) and frozen THF solutions of P5 and P6 at 77 K showed an oxygen isotope sensitive feature around 740 cm⁻¹ which shifts to around 700 cm⁻¹ when using 18O₂ (P4: 741 cm⁻¹, Δ[18O]/Δ[16O] = -40 cm⁻¹; P5: 735 cm⁻¹, Δ[18O]/Δ[16O] = -39 cm⁻¹; P6: 742 cm⁻¹, Δ[18O]/Δ[16O] = -39 cm⁻¹). These values fall in the typical range reported for O···O stretching vibrations of P cores (730–760 cm⁻¹ with Δ[18O]/Δ[16O] of ca. -40 cm⁻¹,19 including oxy-hemocyanin48 and oxy-tyrosinase40). Obviously, the exceptionally long O···O bonds found in P4 and P5 do not translate into unusual rR signatures.28,43

Experimental data for the magnetic coupling in Cu₂O₂ systems determined by SQUID magnetometry are still scarce, mostly because of the thermal lability of such intermediates. Magnetic susceptibility measurements for crystalline material of P4 confirmed the common S = 0 ground state resulting from very strong antiferromagnetic coupling between the cupric ions.44,45

Simulations showed that the lower limit of the exchange coupling is very high, −J ≥ 800 cm⁻¹, based on H = −2JS₁S₂ (Fig. S3†). This is similar to the singlet–triplet splitting observed for oxy-hemocyanin (−J ≥ 300 cm⁻¹)79 and some Cu(μ-η²:η²-O₂)Cu model systems.80,81 In summary, the cationic cores of P4–P6 represent genuine Cu(μ-η²:η²-O₂)Cu species with all their characteristic structural, spectroscopic and magnetic signatures, though with unusually long O···O bonds. Optical features of these complexes are essentially identical when recorded in THF or in a 1 : 1 THF : acetone solution, confirming the integrity of the P cores.

Titration of the purple coloured solutions of P5 or P6 in THF with the base diazabicyclocoundecane (DBU) at low temperatures (193 K) caused a distinct colour change to dark green. Spectral changes were monitored by in situ UV-vis spectroscopy and showed the gradual fading of the bands typical for the P core with the concomitant rise of new bands at 297 nm and 395 nm (Fig. 1a). Full conversion was reached after the addition of about 2 equivalents of DBU per dinuclear copper species, and the resulting products O7 and O8 seemed reasonably stable in the presence of excess DBU. Interestingly, O7 could also be prepared directly from the deprotonated ligand [MeBOX]⁻, which was obtained as an air sensitive white powder by treating MeBOX with one equivalent of nBuLi (see ESI† for details). Reaction of [MeBOX]⁻ with [Cu(MeCN)₄]ClO₄ in THF gave an air sensitive yellow colored solution of the complex [MeBOX]Cu⁺ (characterized by NMR spectroscopy and ESI-MS; see ESI†). Subsequent oxygenation in THF at 193 K yielded a dark green coloured solution with optical features identical to those resulting from the titration experiment starting from P5. This corroborates that DBU serves as a base to abstract the backbone protons of the Me₄BOX capping ligands in P5 (Scheme 2).

In THF solution, O7 and O8 both feature three dominant absorption bands with λmax/nm (ε/M cm⁻¹) around 300 (~2.6 × 10⁴), 335 (~7.8 × 10⁴) and 400 (~10–11 × 10⁴) typical for bis(μ-oxido) dicopper(II) species.80,81 This suggests that peripheral deprotonation of the terminal Me₄HBOX ligand in P5 and

![Fig. 3](image_url)

**Fig. 3** Resonance Raman spectrum of P4 (left) in THF and O7 (right) in THF/pentane (1:1) at 193 K. The ¹⁸O₂ spectra are in black and the ¹⁶O₂ spectra are in red. Residual solvent signals are marked with an asterisk (*).
H, HBOX ligand in $^{\text{p}}6$ triggers conversion of the $^{\text{R}}\text{H}^+\text{P}$ to the $^{\text{R}}\text{O}$ core (Scheme 2). The simulated spectrum of $^{\text{O}}7$ obtained from TD-DFT calculations shows four absorption bands at 310, 340, 400, and 690 nm, which is in pleasant agreement with the experimental spectrum (for a simplified assignment of the two dominant transitions see Fig. 1c, for details the ESI†). Similar optical features have been observed by Herres-Pawlis et al. for a guanidine supported bis(μ-oxido) complex, and these authors arrived at an identical assignment of the electronic transitions underlying the two dominant absorptions.† The band at 690 nm originates from a ligand-to-metal charge transfer with BOX-centered donor MO ($^{690}\text{nm}$ originates from a ligand-to-metal charge transfer with respect to each other (Fig. 4). In line with expectations, the Cu$^{2+}$ species (for which we find the bis(μ-oxido) isomer to be more stable, ESI†) should not be present in solution as it is thermodynamically disfavored against decomposition into $^{\text{p}}5$ and $^{\text{O}}7$.

A DFT assessment of the PO core isomerization for $^{\text{p}}5$ and $^{\text{O}}7$ nicely corroborates the experimental observations (Scheme 3): for $^{\text{p}}5$, the peroxido isomer is found to be more stable than the bis(μ-oxido) isomer $^{\text{O}}7$ by $\Delta G^{193} = 4 \text{ kcal mol}^{-1}$, and is separated from the latter by a barrier of $\Delta G^{193} = 10 \text{ kcal mol}^{-1}$. For the neutral complex $^{\text{O}}7$, a reverse stability order results with $^{\text{O}}7$ being favored by 7 kcal mol$^{-1}$ over $^{\text{p}}7$, and an interconversion barrier of 11 kcal mol$^{-1}$ was computed. Moreover, the computational results indicate that a putative singly (de)protonated species (for which we find the bis(μ-oxido) isomer to be more stable, ESI†) should not be present in solution as it is thermodynamically disfavored against decomposition into $^{\text{p}}5$ and $^{\text{O}}7$.

Addition of common Brønsted acids ([LuH]OTf, [LuH]BF$_4$, and HBF$_4\cdot$Et$_2$O where LuH = lutidinium) to solutions of $^{\text{O}}7$ at 193 K did not trigger back-isomerization to the μ−μ$^2$−peroxido species $^{\text{p}}5$, but led to decomposition instead. However, the reversibility of the equilibrium shown in Scheme 2 was demonstrated by the following experiment: reaction of two equivalents of H, HBOX with one equivalent of [Cu(MeCN)$_4$]ClO$_4$ in THF in the presence of O$_2$ directly led to the formation of the bis(μ-oxido) complex $^{\text{O}}8$. In this case, deprotonation is accomplished by excess H, HBOX acting as a Brønsted base. Similarly, in situ UV-vis monitoring of H, HBOX titration into a solution of $^{\text{p}}6$ (P core) indicated the formation of $^{\text{O}}8$ (O core) (Fig. 5 and S7†). Subsequent titration of [Cu(MeCN)$_3$]ClO$_4$ into the reaction mixture in the presence of excess O$_2$, in turn, resulted in the

![Fig. 4](image_url) Molecular structure of $^{\text{O}}7$ (top view and side view) with 30% probability ellipsoids. Hydrogen atoms and solvent molecules have been omitted for clarity.

![Scheme 3](image_url) Isomerization reactions for $^{\text{p}}5^{\text{ESI}}$ (a) and $^{\text{O}}7$ (b) computed at the BLYP-D3/def2TZVP/SPSSD/COSMO(THF)//PBE-D3/def2TZVP/SPSSD/SMO(THF) level of DFT.
conversion back to $\text{P}^6$ (Fig. 5 and S8†). Thus, re-protonation of the ligand backbone in $\text{P}^8$ is accomplished by $\text{H}^{\text{III},\text{III},\text{BOX}}^+$. This procedure enables complete control of the $\text{P}/\text{O}^r$ interconversion without the need of adding exogenous acids. UV-vis monitoring of the reaction sequence (Fig. 5) confirmed that close to 1 equivalent of $\text{P}^8$ is formed during the first step, and a further 0.25 equivalents of $\text{P}^6$ result after addition of the second equivalent of $[\text{Cu}^{\text{MeCN}}]_3\text{ClO}_4$ (Fig. 5).36

On warming from 193 K to room temperature, the intensely colored solutions of $\text{P}^4$, $\text{P}^5$, and $\text{P}^7$ gradually changed to light blue, indicating decay of the dicopper/dioxygen complexes. IR spectra of the light blue solid material isolated thereafter showed a characteristic OH stretching vibration around 3480 cm$^{-1}$ (Fig. S4†). Single crystals of the material were obtained employing Cu(i) triflate as the metal source, and X-ray crystallography revealed the formation of the dihydroxo complex $[\text{Cu}^{\text{MeCN}}]_3\text{ClO}_4$ (Fig. 6). No degradation or oxygenation of the BOX ligands was observed.

**Fig. 6** Molecular structure of $\text{P}^9$ set at 30% probability. Most hydrogen atoms have been omitted for clarity.

**Conclusions**

In conclusion, we have shown that the peroxydo/bis($\mu$-oxido) interconversion in a $[\text{Cu}_2\text{O}_2]$ complex supported by proton-responsive BOX ligands can be controlled by peripheral (de)protonation events on the ligand backbone. We suggest this system as a bioinorganic mimic for type III dicopper proteins (or the dicopper active site of pMMO) in which the Cu ions are supported by histidine imidazoles, which offer a backside N atom amenable to potential (de)protonation equilibria in response to changes in local pH. In fact, (de)protonation of histidine imidazole ligands in metalloproteins is widely used for tuning redox potentials and electronic structures of the metallocofactors,57,60 and it is an integral part of biologically important proton coupled electron transfer (PCET) reactivity (such as in the Rieske proteins).61 It is an interesting perspective to introduce, via proton-responsive ligands, PCET reactivity to $\text{Cu}_4\text{O}_2$ intermediates. We are currently pursuing further studies in this direction.

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**Notes and references**

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42 Depending on the particular choice of functional, basis set and relativistic approach, DFT optimized structures for the peroxydo isomer show significant variations in the O–O bond length, overall underestimating the experimentally determined value by ~0.13 to ~0.24 Å. Consistently, the O–O stretching vibration is substantially overestimated by 80–355 cm$^{-1}$ compared to experiment, again depending on the DFT approach chosen. As detailed in the ESI,$^1$ the strong method dependence goes back to a very shallow stretching potential along the O–O bond: for example, a relaxed scan of the O–O bond length in $^5$S performed at the BP86/SVP level of DFT from $R_{O-O} = 1.46$ Å (optimized minimum structure) to 1.58 Å (experimental bond length) results in an energy increase of merely 2.2 kcal mol$^{-1}$. Harmonic O–O stretching frequencies, however, computed for these two points vary by an enormous 260 cm$^{-1}$. These findings, together with the fact that the neglect of crystal packing effects and vibrational anharmonicitites further complicate comparison with experiment, forced us to conclude that a quantitative modeling of structural and vibrational characteristics of the peroxydo species studied here is outside the scope of presently available density functional methods.

43 While having a small amount of the O isomer in the crystals (see E. Pidcock, S. DeBeer, H. V. Obias, B. Hedman, K. O. Hodgson, K. D. Karlin and E. I. Solomon, *J. Am. Chem. Soc.*, 1999, **121**, 1870) cannot be completely ruled out, this seems unlikely because (i) free refinement turned out to be unstable when trying to model an O–O disorder in the crystallographic structures; (ii) similar long O–O bonds are observed for both complexes, $^4$P and $^5$S, the latter lacking the ligand backbone proton required for deprotonation-induced transformation to the corresponding bis(μ-oxido) species; and (iii) the rR spectra of both solid materials do not show any isotope sensitive bands at ~600 cm$^{-1}$ that could be assigned to the O isomer.
In good agreement with this experimentally determined lower limit, a broken-symmetry DFT assessment of $P_5$ resulted in $-J = 1080 \text{ cm}^{-1}$ (see Scheme 3 and the ESI†).

For $O_8$ the relative intensity of the bands around 335 and 400 nm is inverted.

Some decomposition occurs, and hence the re-formation of $P_6$ is not quantitative.