*Metal–Radical Complexes*

# An Unprecedented Bridging Phenoxyl Radical in Dicopper(II) Complexes: Evidence for an $S=\frac{3}{2}$ Spin State**

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The cooperativity between a radical and a transition-metal ion in a single molecular entity is demonstrated in highly sophisticated biocatalysts.[1] Galactose oxidase, which has an

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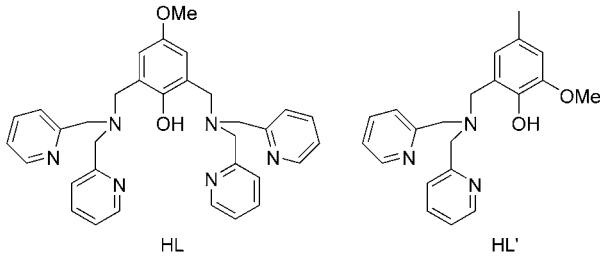
active site composed of a tyrosyl radical magnetically coupled to a cupric ion, nicely exemplifies this synergy. In this example the two redox centers work together to promote the two-electron oxidation of primary alcohols to give aldehydes.[2] For a better understanding of the metal–radical interaction (and its biological relevance), transition-metal complexes involving one or two coordinating radicals have been characterized recently.[3] So far no complexes with a bridging radical have been reported. We describe herein an unprecedented metal–radical system, a dicopper(II) μ-phenoxyl complex. This was achieved using the dicopper(II) complexes of the dinucleating ligand HL. Its oxidative chemistry is compared to that of the copper(II) complex of the mononucleating analogue HL′.




When two equivalents of $Cu(ClO_4)_2{\cdot}6H_2O$ and HL were mixed in acetonitrile in the presence of one equivalent of $NEt_3$, complex $[L(CH_3CN)_2Cu_2]^{3+}$ (**1**) was obtained as its $ClO_4^-$ salt.[4] Its crystal structure (Figure 1) shows that the ligand binds two copper(II) atoms having square-pyramidal geometry through coordination to three nitrogen atoms from the ligand (two pyridyl N atoms and one tertiary amino group) and one from an exogenous acetonitrile molecule. The coordination sphere is completed by an oxygen atom of a μ-phenolato group, which bridges the two metal centers having a separation of 4.06 Å. The use of HL and two equivalents of both $Cu(ClO_4)_2{\cdot}6H_2O$ and $NEt_3$ affords complex $[L(\mu OH)Cu_2]^{2+}$ (**2**) as its $ClO_4^-$ salt.[5,6] Its crystal structure (Figure 1) has been previously reported:[5] the coordination sphere of the copper atoms contains three nitrogen atoms from the ligand (two pyridyl and one tertiary amino group) completed by two oxygen atoms (from one phenolato and one hydroxo groups) which bridge the metal centers. The two copper ions have trigonal-bipyramidal coordination geometry, with a Cu–Cu distance of 2.98 Å. Addition of one equivalent of $Cu(CF_3SO_3)_2$ or $Cu(ClO_4)_2{\cdot}6H_2O$ to HL′ in acetonitrile in the presence of one equivalent of $NEt_3$ affords the dimer $[L'Cu]_2^{2+}$ (**3**) as its $CF_3SO_3^-$ or $ClO_4^-$ salt (Figure 1).[4] In **3** each copper atom is coordinated by two pyridyl nitrogens, one amino nitrogen, and two μ-phenolato oxygens (one from each ligand), and the intermetallic distance is 3.12 Å. This dimer is relatively stable, as reflected by its $K_{py}$ value of 0.297 $M^{-1}$.[7] All the ligands thus afford copper(II) complexes involving at least one coordinating μ-phenolato unit.

The UV/Vis spectra of **1** (Figure 2), **2**, and **3** exhibit a μ-phenolato-to-copper charge-transfer (CT) transition in the region between 450 and 550 nm, and a broad absorption at

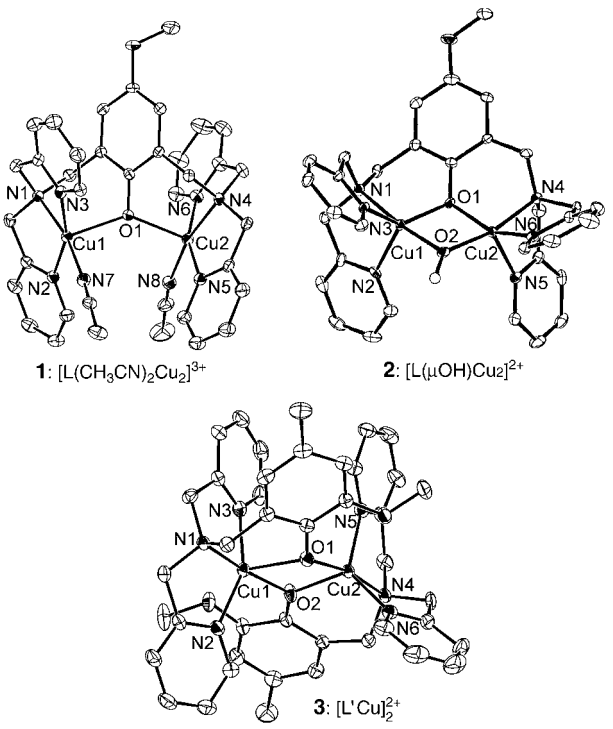



***Figure 1.*** X-ray crystal structures of **1**–**3** (ORTEP diagrams, thermal ellipsoids at the 30% probability level). Selected bond lengths [Å] and angles [°]: $[L(CH_3CN)_2Cu_2]^{3+}$ (**1**): Cu1-O1 2.170(2), Cu2-O1 2.150(2), Cu1-Cu2 4.059(5), Cu1-O1-Cu2 140.0(1); $[L(\mu OH)Cu_2]^{2+}$ (**2**):[5] Cu1-O1 1.997(3), Cu2-O1 2.039(3), Cu1-Cu2 2.980(9), Cu1-O-Cu2 95.2(2); $[L'Cu]_2^{2+}$ (**3**): Cu1-O1 2.077(2), Cu1-O2 1.923(2), Cu2-O1 1.917(2), Cu2-O2 2.303(2), Cu1-Cu2 3.123(5), O1-Cu1-O2 82.72(7), O1-Cu2-O2 77.05(7).

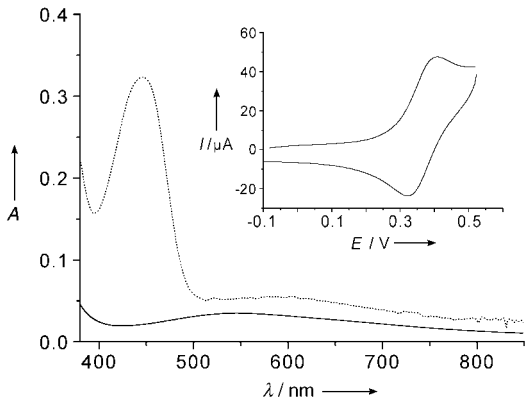



***Figure 2.*** Electronic spectra of 0.1 mM solutions of **1** (solid lines) and electrochemically generated $\mathbf{1}^{\bullet+}$ (dotted lines) recorded in $CH_3CN$ (0.01 M TBAP) at 233 K ($l = 1$ cm). Inset: Cyclic voltamogram (under Ar atmosphere) of **1** (1 mM in $CH_3CN$, 0.1 M TBAP) at 298 K; scan rate: 0.1 $Vs^{-1}$.

higher wavelengths attributed to d–d transitions.[8] The X-band EPR spectrum of **1** in $CH_3CN$ exhibits a $\Delta M_S = \pm 2$ transition at $g = 4.3$, associated with spin triplet resonances at $g = 2.24$ and 1.99, indicating that the two copper(II) atoms are weakly ferromagnetically exchange-coupled. The zero-field splitting (zfs) parameters ($D = 0.036\ cm^{-1}$, $E = 0\ cm^{-1}$) and

$g_{\parallel} = 2.30$, $g_{\perp} = 2.07$ were obtained from simulation. Using the point dipole approximation,[9] we calculated a 4.5-Å separation between the two copper(II) atoms, a value in reasonable agreement with the X-ray structure analysis. Complex **2** is EPR-silent, indicating that the two copper(II) atoms are strongly antiferromagnetically exchange-coupled, due to optimal magnetic orbital overlap.[5] Complex **3** exhibits a ferromagnetic coupling between the two copper atoms similar to that in **1** but with larger zfs parameters ($D = 0.080\ cm^{-1}$, $E = 0.027\ cm^{-1}$, $g_1 = 2.04$, $g_2 = 2.06$, $g_3 = 2.12$), as is expected for a complex with a shorter intermetallic separation. (The complex $[L'(py)Cu]^+$ exhibits a $S_{Cu} = \frac{1}{2}$ signal typical for a mononuclear copper(II) complex).

The cyclic voltammograms of **1** (Figure 2 inset) and **2** in $CH_3CN$ (0.1 M tetrabutylammonium perchlorate (TBAP)) display a reversible one-electron wave in the positive region of potentials ($E_{1/2} = 0.36$ V vs $Fc^+/Fc$, $\Delta E_p = 0.09$ V and $E_{1/2} = 0.45$ V, $\Delta E_p = 0.09$ V for **1** and **2**, respectively), attributed to the oxidation of the μ-phenolato moiety into a μ-phenoxyl radical.[10] This signal is irreversible both for **3** (at $E_p^a = 0.45$ V) and $[L'(py)Cu]^+$ (at $E_p^a = 0.14$ V), showing that the radical evolves on the experiment timescale. Complexes **1**–**3** are thus oxidized in the same potential range, highlighting that the structure of the complex affects weakly the oxidation potential of the μ-phenolato ligand. However, $[L'(py)Cu]^+$ is oxidized at a potential 0.3 V lower, which can be explained by the lower electron density at the oxygen atom of a μ-phenolato ligand compared to that of a phenolate group. In addition, we have previously shown that species such as **3** do not retain their dimeric structure upon oxidation: if they are stable enough to be generated, the phenoxyl radical species evolve towards the corresponding monomers.[11] Thus, only **1** and **2** could be oxidized to give complexes with bridging phenoxyl radicals.

The one-electron-oxidized complexes $\mathbf{1}^{\bullet+}$ and $\mathbf{2}^{\bullet+}$ exhibit similar UV/Vis features: π–π* transitions typical of phenoxyl radicals[12] are observed at 440 nm ($3330\ M^{-1}cm^{-1}$) and 600 nm ($560\ M^{-1}cm^{-1}$) for $\mathbf{1}^{\bullet+}$ (Figure 2), and at 445 nm ($4730\ M^{-1}cm^{-1}$)[13] and 600 nm ($1000\ M^{-1}cm^{-1}$)[13] for $\mathbf{2}^{\bullet+}$. From the decay of the former band, a half-life of 22.3 min was obtained for $\mathbf{1}^{\bullet+}$ at 298 K, and of less than 20 s for $\mathbf{2}^{\bullet+}$ at 290 K.

The 9.4-GHz EPR spectrum of the electrochemically generated $\mathbf{1}^{\bullet+}$ recorded at 4 K (Figure 3) exhibits a $\Delta M_S = \pm 3$ transition at $g = 8$, typical of an $S = \frac{3}{2}$ spin state, whose intensity is proportional to the reciprocal of the absolute temperature ($T^{-1}$). This quartet thus corresponds to the ground state.[14] The zfs parameters $D = -0.056\ cm^{-1}$ and $E = 0.015\ cm^{-1}$ ($g_{\parallel} = 2.142$, $g_{\perp} = 2.039$) were obtained from simulation of both the 9.4-GHz and 115-GHz EPR spectra (Figure 3). The $D$ value is close to that reported for an excited $S = \frac{3}{2}$ spin state in a triangular tricopper(II) complex (−53.5 mT),[15] but significantly different from those reported for organic triradicals ($|0.003–0.008|\ cm^{-1}$)[16] and mononuclear bis(phenoxyl) radical copper(II) complexes ($|0.4|\ cm^{-1}$).[17] The 9.4-GHz EPR spectrum of $\mathbf{2}^{\bullet+}$ exhibits two sets of signals, a weak $\Delta M_S = \pm 3$ transition at $g = 8$ and a dominating $S_{Cu} = \frac{1}{2}$ signal (attributed to a degraded complex containing noninteracting copper(II) nuclei) at $g = 2$.

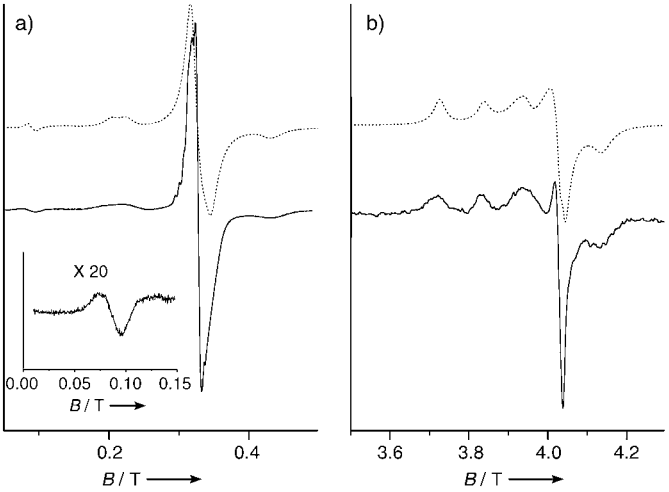



***Figure 3.*** a) X-Band EPR spectrum of electrochemically generated $\mathbf{1}^{\bullet+}$ (1 mM in $CH_3CN$, 0.1 M TBAP): $T = 4$ K, modulation 0.393 mT/100 kHz, frequency 9.44 GHz, power 1 mW. Solid lines: experimental, dotted lines: simulation. b) 115-GHz EPR spectrum $\mathbf{1}^{\bullet+}$ (5 mM in $CH_3CN$, 0.1 M TBAP) at $T = 5$ K. Solid lines: experimental, dotted lines: simulation (parameters are given in the text).

Although the $\Delta M_S = \pm 3$ transition is weak (its intensity decreases as the temperature increases), these results demonstrate that $\mathbf{2}^{\bullet+}$ also exhibits a quartet ground state.

In summary, μ-phenoxyl dicopper(II) complexes in which the two copper(II) and the radical spins are ferromagnetically exchange-coupled could be obtained. Their stability, and thus their reactivity, is finely tuned by both the nuclearity of the complex and the nature of coordinating solvent. Since tyrosyl residues are ubiquitous in metalloenzymes, such species could be biologically relevant. On the other hand, the chemical reactivity of these μ-phenoxyl dicopper(II) species which formally contain "three oxidizing equivalents" constitute a promising and fascinating area for the studies of new chemical properties.

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[3] For reviews see: B. A. Jazdzewski, W. B. Tolman, *Coord. Chem. Rev.* **2000**, *200–202*, 633; S. Itoh, M. Taki, S. Fukuzumi, *Coord. Chem. Rev.* **2000**, *198*, 3; P. Chaudhuri, K. Wieghardt, *Prog. Inorg. Chem.* **2001**, *50*, 151.

[4] Crystal data: for $\mathbf{1}(ClO_4^-)_3 \cdot 0.33\,H_2O \cdot 0.66\,EtOH$: $C_{40.33}H_{46.67}Cl_3Cu_2N_9O_{15}$, purple–blue prisms, monoclinic, space group $P21/c$, $a = 21.322(2)$, $b = 10.920(3)$, $c = 23.131(5)$ Å, $\alpha = 90$, $\beta = 115.41(1)$, $\gamma = 90°$, $V = 4864.5(6)$ Å$^3$, $Z = 4$, $D = 1.544\ g\,cm^{-3}$, $T = 294$ K, $F(000) = 2322.60$, $\mu = 1.114\ mm^{-1}$,

$\lambda(Mo_{K\alpha}) = 0.71073$ Å, 55223 reflections collected, 13287 unique, 8321 reflections ($I > 2\sigma$), $R_{int} = 0.07971$. The final agreement factors are $R_1 = 0.0609$ for data with $F_0 > 2\sigma(F_0)$ and $wR_2 = 0.1006$ for all data. CCDC 244865 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk); for $\mathbf{3}_{1.5}(ClO_4^-)_3$: $C_{63}H_{66}Cl_3Cu_3N_9O_{18}$, brown needles, triclinic, space group $P-1$, $a = 12.605(1)$, $b = 13.213(1)$, $c = 21.692(2)$ Å, $\alpha = 74.5(3)$, $\beta = 86.8(3)$, $\gamma = 67.6(3)°$, $V = 3214(6)$ Å$^3$, $Z = 2$, $D = 1.585$ g.cm$^{-3}$, $T = 150$ K, $F(000) = 1578$, $\mu = 1.188$ mm$^{-1}$, $\lambda(Mo_{K\alpha}) = 0.71073$ Å, 43303 reflections collected, 21243 unique, 16811 reflections ($I > 2\sigma$), $R_{int} = 0.06431$. The final agreement factors are $R_1 = 0.0547$ for data with $F_0 > 2\sigma(F_0)$ and $wR_2 = 0.0763$ for all data. CCDC 245087 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

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[6] Mixing only one equivalent of $Cu(ClO_4)_2 \cdot 6H_2O$ and HL in acetonitrile in the presence of one equivalent of $NEt_3$ did not afford the expected mononuclear copper(II) complex of HL. Instead, **2** was isolated in 40% yield.

[7] Addition of pyridine (py) to **3** induces a dimmer-to-monomer conversion yielding $[L'(py)Cu]^+$. The exogenous pyridine coordinates to the copper instead of one μ-phenolato oxygen. $K_{py} = ([L'(py)Cu]^{+2}/([pyridine]^2[[L'Cu]_2^{2+}])$ was determined by UV/Vis titration from the equilibrium: $[L'Cu]_2^{2+} + 2\,pyridine \rightleftarrows 2\,[L'(py)Cu]^+$.

[8] UV/Vis data ($\lambda_{max}$ (nm), $\varepsilon$ ($M^{-1}cm^{-1}$) in $CH_3CN$: **1**: 547 (350), d–d transitions appear as a broad shoulder; **2**: 447 (330), 805 (190); **3**: 463 (340), 880 (250); $[L'(py)Cu]^+$: 531 (330), 880 (210).

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[10] A linear dependence of $E_{1/2}$ as a function of the μ-phenolate $\sigma^+$ Hammet constant is observed for related compounds (Figure S8 in the Supporting Information). Moreover, the UV/Vis feature of the oxidized species matches well that reported for methoxyphenoxyl–copper(II) complexes (D. Zurita, I. Gautier-Luneau, S. Ménage, J.-L. Pierre, *J. Biol. Inorg. Chem.* **1997**, *2*, 46; Y. Shimazaki, S. Huth, S. Hirota, O. Yamauchi, *Inorg. Chim. Acta* **2002**, *331*, 168). This further confirms that the one-electron electrochemical process is ligand-based rather than metal-based.

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[13] The $\varepsilon$ values are probably under estimated for $\mathbf{2}^{\cdot+}$ due to its low stability.

[14] The 9.4-GHz EPR spectrum of $\mathbf{1}^{\cdot+}$ measured at 215 K lacks most of the transitions associated with the quartet. It still exhibits a signal at $g = 2.06$ that could be attributed to an excited ($S = \frac{1}{2}$) state, indicating that the exchange constant $J$ is weak.

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