Inorganic Chemistry Cite This: Inorg. Chem. XXXX, XXX, XXX-XXX

Article pubs.acs.org/IC

Effect of Monoelectronic Oxidation of an Unsymmetrical Phenoxido-Hydroxido Bridged Dicopper(II) Complex

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Supporting Information

ABSTRACT: A (μ -hydroxido, μ -phenoxido)Cu^{II}Cu^{II} complex 1 has been synthesized using an unsymmetrical ligand bearing an N,N-bis(2-pyridyl)methylamine (BPA) moiety coordinating one copper and a dianionic bis-amide moiety coordinating the other copper(II) ion. Electrochemical mono-oxidation of the complex in DMF occurs reversibly at 213 K at $E_{1/2} = 0.12$ V vs Fc⁺/Fc through a metal-centered process. The resulting species (complex 1^+) is only stable at low temperature and has been spectroscopically characterized by UV-vis-NIR cryo-spectroelectrochemical and EPR methods. DFT and TD-DFT



calculations, consistent with experimental data, support the formation of a Cu^{II}Cu^{III} phenoxido-hydroxido complex. Lowtemperature chemical oxidation of 1 by NOSbF₆ yields a tetranuclear complex $2(SbF_6)(NO_2)$ which displays two binuclear $Cu^{II}Cu^{II}$ subunits. The X-ray crystal structure of $2(SbF_6)(NO_2)$ evidences that the nitrogen of the terminal amide group is protonated and the coordination of the amide occurs via the O atom. The bis-amide moiety appears to be a non-innocent proton acceptor along the redox process. Alternatively, protonation of complex 1 leads to the complex $2(ClO_4)_{2}$, as evidenced by X-ray crystallography, cyclic voltammetry, and ¹H NMR.

INTRODUCTION

Over the past couple of years, there has been a growing interest toward the development of systems capable of stabilizing highvalent copper species.¹ Besides type III dinuclear copper enzymes, e.g., tyrosinase yielding peroxo-bridged $(\mu - \eta^2 - \eta^2)$ -Cu^{II}Cu^{II} species in the presence of dioxygen, which can be converted into reactive $bis(\mu$ -oxo)Cu^{III}Cu^{III} intermediates,²⁻⁵ new types of species have been suggested. This is in relation to advances in oxidation of alkanes by copper-loaded zeolites⁶ as well as in enzymatic systems such as lytic polysaccharide monooxygenases (LPMOs)^{7,8} and particulate methane monooxygenase (pMMO).⁹⁻¹¹ So far for pMMO, the nature and nuclearity of the intermediates involved in activation of the strong C-H bond of methane remain debated, moving recently from a dinuclear copper site^{9,11,12} toward a possible mononuclear site.^{13,14} Nevertheless, from computational analysis, Yoshizawa and co-workers have suggested that the reactivity toward methane could arise from dicopper mixedvalent species such as $bis(\mu-oxo)Cu^{II}Cu^{II}$ or $(\mu-oxo)(\mu-oxo)(\mu-oxo)$ hydroxo)Cu^{II}Cu^{III}.^{12,15,16} Unlike mononuclear Cu^{III} species in the field of bioinorganic chemistry, descriptions of relevant synthetic models are still largely unexplored. Few compounds

have been reported,¹⁷⁻¹⁹ and investigations of their reactivity are limited despite that studies on such mixed-valent Cu^{II}Cu^{III} species are of considerable interest for industrial synthesis. The search for new candidates for strong hydrocarbon functionalization under mild conditions is required to produce useful chemical products with low energy costs and high selectivity.²⁰ Our objective was to characterize this type of mixed-valent species starting from an unsymmetrical bimetallic copper(II) complex, designed with a moiety able to stabilize copper(III) and featuring a short Cu-Cu separation. One of the most extensively employed compartmental ligands capable of bringing two copper ions in close proximity is the family of phenoxido-bridged ligands bearing two coordinating arms. Numerous Cu^{II}Cu^{II}-phenoxido bridged complexes have been reported in the literature,²¹⁻²⁴ but few studies have been carried out on the mono-oxidation of such dicopper complexes.^{25–27} Since this monoelectronic oxidation could occur either on the ligand or on the metal ion, specific design is necessary to control the location of the oxidation process.

Received: July 27, 2018

Mono-oxidation processes yielding a phenoxyl radical in accordance with a ligand-centered oxidation have been reported.²⁷ However, very recently, we have described an interesting feature from a series of phenoxido-hydroxido-bridged dicopper(II) species. Upon electrochemical mono-oxidation, the unsymmetrical environment in the complex bearing the ligand 2-[bis(2-pyridylethyl)-aminomethyl]-6-[bis(2-pyridylmethyl)-aminomethyl]-4-methylphenol (CH₃-BPMEP)²⁸ (Chart 1) supported the formation of a transient





 $Cu^{II}Cu^{II}$ species, demonstrating a metal-centered oxidation. Subsequently, this intermediate species evolved toward a dicopper(II,II) phenoxyl radical species.²⁵ Following these studies, in the present work, we explore the coordination chemistry of a novel unsymmetrical phenoxido bridge scaffold designed with the aim of providing two distinct binding sites to stabilize a $Cu^{II}Cu^{III}$ mixed-valent species. The synthesized ligand (H₃L) contains one bis(2-pyridylmethyl)aminomethyl arm suited for the Cu^{II} redox state and a bis-amide arm which can be deprotonated for stabilizing the Cu^{III} redox state, these two moieties being connected through a phenoxido spacer (Scheme 1). Amidates^{29,30} are indeed strongly donating ligands in the family of anionic ligands (corroles,³¹ thiolates,³² oxamates³³), hence are fully appropriate to lead to highly stabilized Cu(III) species as requested.

EXPERIMENTAL SECTION

General. NMR spectra were recorded on a Bruker AM 300 (1 H at 300 MHz, 13 C at 75 MHz) or a Bruker Avance (1 H at 400 MHz, 13 C at 100 MHz). Chemical shifts are given relative to solvent residual peak.

X-band EPR spectra were recorded at 100 K with an EMX Bruker spectrometer equipped with a standard ER4102ST Bruker cavity. At helium temperature, the spectrometer is equipped with an ER4116DM Bruker cavity, a, ESR900 continuous-flow Oxford

Scheme 1. Synthetic Route for the Ligand H₃L

Instrument cryostat, and an ER4131VT Bruker temperature controller. All spectra presented were recorded under nonsaturating conditions. Simulation of EPR spectra was carried out with EasySpin software.

UV-vis absorption spectra were obtained by using a Varian Cary 50 spectrophotometer operating in the 200-1000 nm range with quartz cells. It was equipped with a Hellma low-temperature immersion probe (1 cm path length quartz cell) for experiments at low temperatures. The temperature was controlled with a Lauda RK8 KS cryostat.

Electrospray mass spectra were recorded on an Esquire 3000 plus Bruker Daltonics with nanospray inlet.

Room temperature electrochemical studies of the copper complex were performed in a glovebox (Jacomex) ($O_2 < 1$ ppm, $H_2O < 1$ ppm) with a home-designed 3-electrodes cell (WE: glassy carbon (GC) or platinum, RE: Pt wire in a 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 software. Dimethylformamide (DMF) was purchased from Acros. The supporting salt NBu₄ClO₄ (99%) was purchased from Sigma-Aldrich and stored as received in the glovebox.

Low-temperature voltammetry and thin-layer UV–vis–NIR spectroelectrochemistry were performed with specific home-designed cells (WE: Pt or GC, RE: Pt wire, CE: Pt wire) inside a glovebox. Cooling down of the solution was operated with a Lauda Pro-line cryostated system. Some low-temperature experiments were completed at a temperature close to the freezing point of DMF, but because of the presence of high concentrations of electrolyte and dissolved complex, the freezing point is lower compared to a pure solution of DMF. The UV–vis and vis–NIR optic fiber probes were purchased from Ocean Optics. Time-resolved UV–vis detection was performed with QEPro and NIR-Quest spectrometers (Ocean Optics).

Syntheses. Synthesis of 3-(Chloromethyl)-2-hydroxy-5-methyl-salicylic Acid. 5-Methylsalicylic acid (5 g, 0.033 mol) was suspended in concentrated HCl (37%) (55 mL), and a solution of formaldehyde (37%) (5 mL) was added. The mixture was stirred at reflux during 2 h 30 min. The resulting suspension was diluted in water and filtered through a porous frit. The white solid was 3 times rinsed with water. After drying under vacuum overnight, 6.23 g of white solid was isolated. Yield 95%. ¹H NMR (CDCl₃, 300 MHz): δ (ppm) 10.66 (s, 1H), 7.71 (d, *J* = 1.2 Hz, 1H), 7.45 (d, *J* = 1.4 Hz, 1H), 4.68 (s, 2H), 2.32 (s, 3H). ¹³C NMR (CDCl₃, 75 MHz) δ (ppm) 173.9, 158.2, 138.7, 131.3, 128.8, 125.9, 111.2, 40.7, 20.5.

Synthesis of Ligand (H_3L). To the mixture of bis(2-pyridylmethyl)amine (BPA) (4 g, 0.02 mol) and potassium carbonate (19.4 g, 0.14 mol) in CH₃CN (100 mL) was added 3-(chloromethyl)-2hydroxy-5-methylsalicylic acid (4.2 g, 0.02 mol) in CH₃CN (50 mL). The mixture was refluxed overnight under N₂. The resulting reaction mixture was cooled at RT, and filtered through a porous frit. The



filtrate was recovered and evaporated to dryness. The crude product was used without any further purification. ¹H NMR (DMSO-d6, 300 MHz): δ (ppm) 8.47 (ddd, J1 = 4.9 Hz, J2 = 1.6 Hz, J3 = 0.9 Hz, 2H) 7.76 (td, $J_1 = 7.7$ Hz, $J_2 = 1.8$ Hz, 2H), 7.63 (dt, J = 7.8 Hz, $J_2 = 0.8$ Hz, 2H), 7.22 (ddd, J1 = 7.4 Hz, J2 = 4.9 Hz, J3 = 1.2 Hz, 2H) 7.40 (d, J = 2.5 Hz, 1H), 7.17 (d, J = 2.3 Hz, 1H), 3.72 (s, 4H), 3.58 (s, 2H), 2.17 (s, 3H). In a Schlenk flask, the previous compound was dissolved in dry CH₂Cl₂ and degassed. Then 3 equiv of triethylamine were added and the mixture was cooled to 0 °C. One equivalent of N,N-dimethylmethaniminium hexafluoro-phosphate (HATU) was dissolved in 3 mL of dry DMF and added to the mixture. A white precipitate appeared. After 1 h at 0 °C, a solution of glycine Nmethylamide (1.3 equiv) in dry CH₂Cl₂ was added dropwise at 0 °C. After the addition, the cooling bath was removed and the reaction mixture was stirred overnight at 20 °C. A white solid formed was removed by filtration and washed with CH₂Cl₂. The mixture was evaporated to dryness; the residue was dissolved in EtOAc and washed with a saturated solution of NaCl. The organic layer was dried over Na2SO4 and evaporated. The resulting crude product was purified by column chromatography on silica using acetone as an eluent. The pure ligand was crystallized from a CH₂Cl₂-diethyl ether solution and isolated as a light beige powder. Overall yield: 34%. ¹H NMR (CDCl₃, 300 MHz): δ (ppm) 9.16 (t, J = 5.5 Hz, 1H), 8.59 (d, J = 4.4 Hz, 2H) 7.87 (d, J = 1.5 Hz, 1H), 7.66 (td, J = 7.3 Hz, J = 1.5 Hz, 2H), 7.30 (d, J = 7.8 Hz, 2H) 7.21 (dd, J = 7.6 Hz, J = 5.3 Hz, 2H), 7.03 (d, J = 1.8 Hz, 1H), 6.71 (s, 1H), 4.17 (d, J = 6.0 Hz, 2H), 3.92 (s, 4H), 3.84 (s, 2H), 2.82 (d, J = 4.8 Hz, 3H), 2.27 (s, 3H). ¹³C NMR (CDCl₃, 75 MHz) δ(ppm) 170.9, 167.5, 157.7, 154.7, 149.1, 137.1, 135.0, 131.2, 128.5, 123.8, 123.4, 122.6, 118.8, 59.0, 56.8, 44.7, 26.3, 20.4. UV-vis (DMF): λ (ϵ , M⁻¹ cm⁻¹) = 313 (4700) nm; HRMS - ESI/QTOF: m/z [L + H]⁺ calcd 434.2192; found 434.2188; elemental analysis calc. (%) for C₂₄H₂₇N₅O₃·0.25H₂O: C 65.81, H 6.33, N 15.99, found (%): C 65.81, H 6.48, N 16.19.

Synthesis of $[Cu_2(L)(\mu-OH)](1)$. The ligand H₃L (0.150 g, 0.35 mmol) was dissolved in methanol (6 mL), and 4 equiv of tetramethylammonium hydroxide (25% wt methanolic solution, 1.4 mmol) was added. An immediate color change to red was observed. A solution of $Cu(ClO_4)_2 \cdot 6H_2O(0.263 \text{ g}, 0.71 \text{ mmol})$ in MeOH (5 mL) was added to the previous solution of ligand, which resulted in an immediate precipitate. The appearing precipitate was filtered off and the solution was evaporated to dryness. Then, by adding 4 mL of THF, the remaining NMe₄ClO₄ was completely extracted. The brown product was filtered, washed with acetone, and dried under vacuum. Single crystals were obtained by slow diffusion of acetone into a concentrated solution of complex in water. Yield: 0.113 g, 57%. A recrystallization was done by slow diffusion of ethyl acetate into a concentrated solution of previous crystals in DMF. UV-vis (DMF): λ $(\varepsilon, M^{-1} \text{ cm}^{-1}) = 313 \text{ (sh, 5900), 460 (780), 723 (140), 798 (150)}$ nm; elemental analysis calcd (%) for C24H25Cu2N5O4·3.5H2O: C 45.21, H 5.06, N 10.98; found (%): C 45.39, H 5.02, N 10.96.

Synthesis of $[(Cu_2(LH)(\mu-OH))_2](ClO_4)_2 \cdot DMF \cdot EtOAc)$ (2(ClO₄)₂· DMF·EtOAc). Complex 1 (7.9 mg, 0.012 mmol) was dissolved in 3 mL of DMF, and 1 equiv of HClO₄ (0.1 M) was added. The brown solution turned immediately to green after the addition of perchloric acid. Single blue crystals were obtained by slow diffusion of ethyl acetate into the concentrated solution prepared in DMF. Yield: 3.8 mg, 48%. UV-vis after dissolution of the crystals (DMF): λ (ε , M⁻¹ cm⁻¹) = 315 (11600), 410 (sh, 850), 700 (100), 820 (170) nm; ESI-MS: m/z [(Cu₂(LH)(μ -OH))₂ + ClO₄]⁺ calcd 1249.06; found 1248.92.

Safety Note. *Caution!* Although no problems were encountered during the preparation of the perchlorate salts, suitable care should be taken when handling such potentially hazardous compounds.

Crystal Structure Determination and Refinement. Measurements for 1 DMF and $2(\text{SbF}_6)(\text{NO}_2)$ solvate were made on a Bruker-Nonius Kappa diffractometer with an APEXII detector and a multilayer mirror monochromatized Mo(K α) radiation (λ = 0.71073 Å) from an Incoatec microsource at 200 K. The data were collected with phi and omega scans. Data were integrated and corrected for Lorentz and polarization factors with Eval 14, then corrected for absorption with SADABS and merged with Xprep. Crystallographic structures were solved using charge flipping methods implemented by Superflip. C, N, O, S, Cl, and Cu atoms were refined anisotropically by the full matrix least-squares method using ShelxL-2013 run under Olex2. H atoms were calculated on idealized positions and constrained on their bearing atoms.

Measurements for $2(\text{ClO}_4)_2$. DMF·EtOAc were undertaken at the ESRF ID23_1 beamline on a Maatel mini-diffractometer (MD2M) with a DECTRIS Pilatus_6M_F detector and a Silicon 111 monochromatized radiation ($\lambda = 0.72932$ Å) at 100 K. The data were collected with mxCuBE in phi scan mode and integrated and corrected for Lorentz and polarization factors with XDS, then corrected for absorption with SADABS and finally merged with Xprep. The crystallographic structure was solved and refined as above. There are many noticeable things concerning this structure: the crystal is a twin with roughly a 75%–25% ratio. Surprisingly enough, there is a pseudo inversion center located at 0.354 0.500 0.682, giving rise to strong correlations. We believe that the combination of the twin together with this pseudo inversion center could explain why we observe high electronic density residues around the copper ions.

The crystal data of 1·DMF, $2(SbF_6)(NO_2)$ ·solvate, and $2(ClO_4)_2$ · DMF·EtOAc and details of the data collections are given in Table S1. Supplementary data are available from the CCDC, quoting the deposition numbers CCDC 1578061, 1578062, and 1578063 for 1· DMF, $2(SbF_6)(NO_2)$ ·solvate, and $2(ClO_4)_2$ ·DMF·EtOAc, respectively.

Computational Section. All calculations were performed using the Gaussian 09 package.³⁴ To compute oxidation potential value, a calibration (choice of the functional, basis set) was already done on similar systems.²⁵ Geometry optimizations were carried out using the hybrid exchange-correlation PBE0 functional accounting for CH_3CN solvation effects using the IEFPCM continuum solvent model. A mixed basis set composed of the Def2-TZVPD for copper atoms, the 6-311+G(d,p) for N and O atoms, and 6-311G(d,p) for C and H atoms was used. Then energetic calculations were carried out from additional single point calculations on the previously optimized geometries using the M11-L functional and always the IEFPCM continuum solvent model and the same basis set as stated above.

TD-DFT calculations were performed using the functional wB97XD associated with the IEFPCM solvent model and the same basis set as described above. Benchmarks were already done on similar systems.¹⁸ Solutions for the 50 lowest states were computed at this level. For the calculations, different spin states are possible. The ground state of dicopper (II,II) complexes can be either a triplet or a singlet state. For the mono-oxidized species, according to the oxidation site, only a doublet state (oxidation on a copper atom) or a doublet state and quartet state (oxidation on the ligand) were possible. Thus, we have first considered calculations on a doublet state to determine the oxidation site. Mulliken populations and spin densities have allowed us quickly to perform this task. To compute the oxidation potential value when oxidation occurs on the ligand, since two spin states are possible, we consider the high spin state, i.e., the quartet state. Similarly, for the dicopper (II,II) complexes, energy of the triplet state is used even if it is not necessarily the ground state. It is justified since the energy difference between spin states is very small compared to that between two redox states.

RESULTS AND DISCUSSION

Ligand and Complex Synthesis. The preparation of the dinucleating ligand is obtained in a three-step reaction starting from 5-methylsalicylic acid (Scheme 1). The reaction of the 5-methylsalicylic acid with paraformaldehyde in hydrochloric acid gave the corresponding chloromethylated product quantitatively. The N-alkylation of N,N-bis(2-pyridyl)-methylamine (BPA) and the subsequent peptide coupling reaction with the glycine N-methylamide afforded the ligand H₃L as a crystalline material with a global yield of 34% (Figures S1–S3). The dinuclear copper(II) complex 1 was

prepared in 57% yield by the successive addition of 4 equiv of tetramethylammonium hydroxide to a solution of the ligand H_3L in methanol, followed by the addition of 2 equiv of $Cu(ClO_4)_2$ ·6 H_2O .

Description of the Crystal Structure. Crystals suitable for X-ray diffraction of the complex were obtained by slow diffusion of ethyl acetate into a solution of the complex solubilized in dimethylformamide (DMF) at RT. The crystal obtained of $[Cu_2(L)(\mu$ -OH)] ·DMF (1·DMF) contains one associated solvent molecule. The structure of complex 1·DMF reveals that the ligand is deprotonated three times and that the copper centers are doubly bridged by the phenoxido and by a hydroxido group leading to a neutral complex (Figure 1). The



Figure 1. Crystal structure of complex 1 $[Cu_2(L)(\mu$ -OH)] crystallized in DMF/EtOAc with selected numbering scheme. All hydrogen atoms have been omitted for clarity except the hydroxido hydrogen.

unsymmetrical ligand confers different coordination environments for the copper centers. Cu1 is tetracoordinated by oxygen atoms from the phenoxido (O1) and hydroxido (O2) bridges, and by the two deprotonated amide groups (N2, N3), forming a distorted square planar geometry around Cu1 with the angle between the N2-Cu1-O1 and N3-Cu1-O2 planes of 14.5°. On the other hand, the Addison parameter³⁵ (τ) of the pentacoordinated Cu2 is 0.59, indicating that the geometry is a distorted trigonal bipyramid with N1 and O2 occupying the axial positions. The intermetallic distance is 3.007 Å, and the bond distances observed in complex 1 are in agreement with those found in copper(II) complexes coordinated by similar N,O-donor groups.¹³⁶⁻³⁸ Interestingly, within the bisamide core, the C=O bonds decrease (the C7-O3 and the C11-O4 bonds of 1.266 and 1.251 Å, respectively) while the C-N ones lengthen (the C7-N2 and the C11-N3 of 1.335 and 1.328 Å, respectively), indicating a double bond character for the carbonyl groups. Selected bond distances and angles are given in Table 1. Considering the angles, a dihedral angle of 44.4° exists between the Cu1-O1-Cu2 and the plane containing the phenyl ring of the spacer, indicating that the ligand is relatively twisted.

Infrared Spectra. The FT-IR spectra in the solid state of the ligand H₃L and the complex 1 show some differences (Figures S4 and S5). An intense band at 3276 cm⁻¹ is observed for the free ligand H₃L which indicates the presence of an N-H stretching band of the amide groups.³⁹ This band disappears in the spectrum of the complex, supporting the deprotonation of these amide groups. Furthermore, shifts are observed for the stretching vibrations $v_{C=0}$ from the protonated ligand to the complex. These bands corresponding to the two vibrational

Table 1. Selected Bond Lengths and Angles for Complex 1

bond lengths (Å) and angles (deg)					
Cu1-01	1.960(2)	Cu2-N4	2.036(3)		
Cu1-N2	1.914(3)	Cu2-N5	2.043(3)		
Cu1-O2	1.925(2)	C7-N2	1.335(4)		
Cu1-N3	1.928(3)	C7-O3	1.266(4)		
Cu2-O1	2.118(2)	C11-N3	1.328(4)		
Cu2-O2	1.903(2)	C11-O4	1.251(4)		
Cu2-N1	2.024(3)				
O1-Cu1-N2	91.40(11)	O1-Cu2-N5	103.68(10)		
O1-Cu1-O2	81.54(10)	O2-Cu2-N1	171.05(11)		
O1-Cu1-N3	167.29(11)	O2-Cu2-N4	102.77(12)		
N2-Cu1-O2	167.66(12)	O2-Cu2-N5	97.85(12)		
N2-Cu1-N3	85.82(12)	N1-Cu2-N4	82.95(12)		
O2-Cu1-N3	103.23(11)	N1-Cu2-N5	82.52(12)		
O1-Cu2-O2	78.06(9)	N4-Cu2-N5	134.46(11)		
O1-Cu2-N1	93.15(10)	Cu1-O1-Cu2	94.92(9)		
O1-Cu2-N4	120.03(10)	Cu1-O2-Cu2	103.55(12)		

modes $v_{C=0}$ are located at 1675 and 1638 cm⁻¹ for the free ligand and at 1608 and 1564 cm⁻¹ for the complex.

Solution Studies of Complex 1. *UV*–*vis Spectroscopy.* The electronic spectrum of this complex was recorded in DMF and is shown in Figure S6. A shoulder observed at $\lambda = 313$ nm ($\varepsilon = 5900 \text{ M}^{-1} \text{ cm}^{-1}$) can be attributed to the $\pi \rightarrow \pi^*$ transition of the ligand. In the visible region, a broad band at $\lambda = 460 \text{ nm}$ ($\varepsilon = 780 \text{ M}^{-1} \text{ cm}^{-1}$) that dominates can be assigned to a pair of different overlapping LMCT transitions between the phenoxido and copper ions and between the hydroxido and copper ions, according to previous studies.^{38,40} These transitions are responsible for the brown color of the solution. At lower energy, d–d transitions are also present at 723 and 800 nm ($\varepsilon = 140 \text{ M}^{-1} \text{ cm}^{-1}$ and $\varepsilon = 150 \text{ M}^{-1} \text{ cm}^{-1}$).^{41–43}

¹H NMR Spectroscopy. The spectrum of complex 1 was recorded in DMF- d_7 and exhibits paramagnetically shifted resonances within the range -60 to 90 ppm. The chemical shifts are attributed by reference to the spectrum of the symmetrical complex [Cu₂(BPMP)(OH)](ClO₄)₂ previously reported^{44,45} and by the two-dimensional COSY ¹H NMR performed in the range of -5 to 30 ppm (Figures S7 and S8).

Electrochemistry. Cyclic voltammetry (CV) of complex 1 was recorded in DMF containing tetra-n-butyl ammonium perchlorate (NBu₄ClO₄) as the supporting electrolyte (0.1 M). At room temperature (T = 293 K), three oxidation peaks were detected at $E_{pa} = 0.19$, 0.64, and 0.84 V vs Fc⁺/Fc (Figure 2A). The first system is irreversible at low scan rates, but becomes quasi-reversible when the scan rate (ν) is increased ($\nu > 0.5 \text{ V}/$ s) (Figure S10). This behavior is typical of an EC mechanism (E = electrochemical, C = chemical), for which a rather slow chemical process follows the electrochemical oxidation. Lowering the temperature to 213 K induced a modification of the redox behavior as shown by cyclic voltammetry (Figure 2A,B). Indeed, the first system became fully reversible at $E_{1/2}$ (1) = 0.12 V vs Fc⁺/Fc (ΔE_p = 75 mV at ν = 0.1 V/s). Increase of the scan rate (0.02 V/s $< \nu < 1$ V/s) resulted in an increase of peak current and peak separation, without loss of chemical reversibility (Figure S11A). At more positive potential values, a single irreversible system was detected at $E_{pa} = 1.01$ V (Figure 2A). When scanning toward negative potential values, CV displayed a quasi-reversible system at $E_{1/2}(2) = -1.27 \text{ V} (\Delta E_p)$ = 91 mV at v = 0.1 V/s) (Figure 2B). When comparing the reduction and the oxidation processes (Figure 2B), both



Figure 2. CVs of complex 1 in DMF/NBu₄ClO₄ 0.1 M (C WE, E/V vs Fc⁺/Fc): (A) at two different temperatures (T = 293 and 213 K) on the -1.8 to 1.2 V potential range ($\nu = 0.1$ V/s); (B) CV at 0.1 V/s at T = 213 K for the first oxidation and reduction processes.



Figure 3. (A) RDEVs of complex 1 in DMF/NBu₄ClO₄ 0.1 M (C WE, *E*/V vs Fc⁺/Fc) at T = 233 K ($\omega = 600$ rpm, v = 0.05 V/s) before (black) and after (red) low-temperature electrolysis ($E_{app} = 0.25$ V vs Fc⁺/Fc). (B) X-Band EPR spectrum of complex 1 after 1 h electrolysis, T = 10 K. Black: experimental, Blue: Simulated. See text for simulated EPR data.

display the same peak heights by CV (Figure 2B) and Rotating Disk Electrode Voltammetry (RDEV) (Figure S11B). This indicates that oxidation and reduction of complex 1 involve the same number of electrons (*n*). The determination of *n* was carried out by a combination of different electrochemical methods (CV, RDEV (Figure S12) and CA (chronoamperometry, Figure S13)) at room temperature, as previously done for an analogous species.¹⁸ This calculation was performed in the frame of an EC mechanism, as detected by CV at 293 K (see SI for details). The three techniques converge toward *n* = 1, which sounds reasonable considering the unsymmetrical topology of the ligand and assuming that oxidation/reduction processes occur on the metal ions. Thus, electrochemical studies suggest that complex 1 is monoelectronically oxidized at $E_{1/2}$ (1) and monoelectronically reduced at $E_{1/2}$ (2).

Electrochemical Generation and Characterization of the One-Electron Oxidized Species 1⁺. Attempts to prepare the one-electron oxidized species by exhaustive electrolysis of a solution of complex 1 at low temperature (T= 233 K) were carried out. After 1 h, low-temperature RDEV of the solution confirmed that concentration of 1 has decreased, and the presence of a small cathodic wave at $E_{1/2}(1)$ indicates that the one-electron species 1⁺ was formed in solution (Figure 3A). X-band EPR characterization of the electrolyzed solution displayed a weak axial signal at g = 2 with a four-line pattern at 10 K (Figure 3B) while no EPR signal was observed in frozen solution of DMF (X band at 6 and 100 K) for complex 1.^{38,46} Simulation of the experimental result provided the following parameters: $g_{\parallel} = 2.246$, $g_{\perp} = 2.0575$, A_{\parallel} $= 193 \times 10^{-4} \text{ cm}^{-1}$, $A_{\parallel}(^{14}\text{N}) = 17 \times 10^{-4} \text{ cm}^{-1}$, which are typical of a mononuclear Cu(II) center. These results support electrochemical oxidation of one Cu(II) ion into an EPR silent Cu(III) ion, leading to a localized mixed-valent $Cu^{II}Cu^{III}$ complex $\mathbf{1}^{\scriptscriptstyle +}$ similar to the examples previously reported. $^{17-19}$ This transient species decomposed rapidly. CV of the solution was also recorded after electrolysis at low temperature. A new anodic wave was detected at E_{pa} (3) = 0.58 V vs Fc⁺/Fc in addition to the first anodic oxidation at $E_{1/2}$ (1). All these data are consistent with the conclusion that the electrochemically generated mono-oxidized complex 1⁺ evolves toward a new species at 233 K, and can be oxidized at E_{pa} (3).

Cryo-spectroelectrochemical Studies of Complex 1. To further investigate the electrochemical oxidation of complex 1, we employed a cryo-spectroelectrochemical setup which allows the generation and characterization of transient species in a thin layer (optical path = $200 \ \mu$ m) at the electrode surface. This method offers the advantage of characterizing the generated species quickly (a few seconds) which is of interest



Figure 4. (A) 3D UV–vis spectroscopic monitoring of the electrochemical oxidation of complex 1 in DMF/NBu₄ClO₄ at T = 213 K under thinlayer conditions (200 μ m). The red curve represents the current intensity (*i*) response (vs time) upon variation of potential. (B) 2D differential (vs initial spectrum) spectroscopic response of complex 1 upon electrochemical oxidation. The red curves on the right panels represent the variation of the current intensity (*i*) and potential (*E*) with time.



Figure 5. Spin density (purple) plots of 1 (A) (triplet state), 1b⁺ (B) (doublet state), 1a⁺ (C) (quartet state).

when the generated species is not very stable, even at low temperatures, as found for complex 1. Figure 4A displays the UV-vis monitoring of the complex 1 upon electrochemical oxidation by CV (red curve) at T = 213 K. Clearly, when electrochemical oxidation occurs, an increase was observed of the band at around 400 nm. This band decreased when the potential was swept back to its initial value. An important point here is that the redox process is fully reversible as attested by the CV shape, meaning that the species detected by UV-vis spectroscopy is effectively the one-electron oxidized complex 1⁺. In order to better analyze the variation of the spectroscopic data with applied potential, we extracted the initial UV-vis spectrum (t = 0 s) from the set of data. The resulting UV-vis spectra are displayed in a 2D manner in Figure 4B, together with the applied potential and resulting current (red curves). It shows the appearance of a band at λ_{max} = 386 nm at approximately 17 s, which corresponds to the foot of the reduction wave (i.e., before the electrochemically generated 1⁺ gets reduced). This band can be confidently ascribed to a UV feature of the one-electron oxidized species 1⁺.

Theoretical Calculations. In an effort to characterize the species formed during the electrochemical oxidation of 1, theoretical calculations were performed. For the mono-oxidized species, oxidation can occur on the ligand or on one copper(II) atom. In the first case, the ligand-centered radical species $1a^+$, the spin state of the system can be a doublet or quartet state, while, in the other case, the Cu^{II}Cu^{III} mixed-valent species $1b^+$, it is a doublet state. Table S3 gives

the primary computed geometric parameters and Figure 5 the spin-density plots (the difference between the α and the β densities) for 1, 1a⁺, and 1b⁺. Comparisons of the spin densities clearly indicate that oxidation occurs for $1a^+$ on the phenoxido and for $1b^+$ on one copper atom. Values of the oxidation potential of complex 1 associated with, respectively, $1a^+$ and $1b^+$ are computed at the M11-L/IEFPCM level using the protocol already published.²⁵ Theory predicted a standard potential for $1b^+/1$ equal to 0.10 V vs Fc⁺/Fc (and 0.54 V for $1a^{+}/1$). Compared to the experimental data ($E_{1/2}(1) = 0.12$ V vs Fc^+/Fc), $1b^+$ appears as the best description for the monooxidation species. Then we performed for $\mathbf{1b}^+$ time-dependent (TD-DFT) calculations and compared them with the UV-vis spectra of 1⁺. Different benchmarks for TD-DFT calculations were already done on similar systems,¹⁸ and good results were obtained at the wB97XD/IEFPCM level of theory. The main absorption bands are given in Table 2. A transition at $\lambda = 385$

Table 2. TD-DFT Data for the Main Absorption Bands (Oscillator > 0.01 and Weak Spin Contamination) of 1b⁺ (Doublet State) at wB97XD/IEFPCM Level

system	excited state	energy (nm)	oscillator strengths (f)	spin contamination $\langle S^2 \rangle$
1b+	16	386	0.026	0.85
	17	385	0.034	0.83
	18	376	0.019	0.82
	24	347	0.026	0.85

nm with a correct value of oscillator strength (0.0340) and a weak spin contamination ($S^2 = 0.831$ against 0.75 for a doublet state) was found for $1b^+$. This is in agreement with the band at $\lambda = 386$ nm observed by cryo-spectroelectrochemical studies. Natural transition orbital analysis describes this band as a ligand-to-metal charge transfer essentially between the phenoxido ligand and the Cu^{III} ion (Figure 6). All of these



Figure 6. Natural transition orbitals of the excited state of $1b^+$ associated with the absorption band detected by cryo-spectroelectrochemical studies.

results support the formation of a mixed-valent Cu^{II}Cu^{III} species for the mono-oxidized species in agreement with the mono-Cu^{II} signature observed in EPR. Furthermore, a close inspection in the NIR wavelength range shows no appearance of any new band. The lack of NIR band and the observed EPR feature are in accordance with a class I mixed-valent species in the Robin–Day classification.⁴⁷

Chemical Oxidation of Complex 1. In order to better understand the oxidative processes, chemical oxidation was performed by using NOSbF₆ as oxidizing agent in a DMF solution of **1** at T = 243 K. After addition of 1 equiv of the oxidant, the brown solution turned immediately to green. No UV-vis absorptions associated with a transient species could be detected (Figure S14). From the final solution, crystals suitable for X-ray diffraction were obtained by slow diffusion of ethyl acetate into a solution of the oxidized complex **1** in DMF.

Description of the Crystal Structure of Complex 2 Obtained after Chemical Oxidation of the Complex 1. Single crystals of complex 2 were obtained as $[(Cu_2(LH)(\mu OH)_{2}](SbF_{6})(NO_{2})\cdot solvate (2(SbF_{6})(NO_{2})\cdot solvate) where$ solvate = $1.54(C_4H_8O_2)\cdot 0.16(H_2O)$. The nitrite anion present in the crystal structure of complex $2(SbF_6)(NO_2)$ solvate comes from the nitrosonium added in as an oxidant and acts as a counteranion. The structure consists of a tetranuclear complex which can be described as two dinuclear units connected together at an average distance of 2.6 Å to form an opened cubane (Figure 7). Moreover, the equatorial pyridine rings of each dimer are facing each other separated by interplanar distances consistent with the existence of a $\pi - \pi$ interaction which contributes to the stability of the tetranuclear complex. Unlike the initial complex, the ligand is deprotonated twice and the terminal amide function remains protonated.





Figure 7. Molecular structure of the dication 2 obtained after chemical oxidation of 1. Hydrogen atoms (except for the hydroxido bridge and the amide arm), solvent molecules, and counteranions were removed for clarity.

The copper centers are doubly bridged by the phenoxido and by a hydroxido group, leading to a distance of 2.9014 and 2.8936 Å between the Cu1A…Cu2A and Cu1B…Cu2B copper centers, respectively. The polyhedron of coordination around Cu1A and Cu1B is a distorted square pyramid with the copper coordinated by the N atom from the amide groups (N2A, N2B) and also the O atom from the other amide groups (O4A, O4B), by the oxygen of the phenoxido (O1A, O1B) and hydroxido (O2A, O2B) groups. However, a close examination of the coordination around Cu2A and Cu2B indicates that these two copper centers have different geometries. A distorted square pyramid for Cu2A and a distorted octahedron for Cu2B explains why we have an opened cubane as a resulting structure for this complex. The distance between Cu2A and O2B is quite long at 2.823 Å, which does not allow a coordination between these two atoms. Selected bond distances and angles are given in Table 3. On the bis-amide side, although the terminal amide has been reprotonated and coordinates the metal center by the oxygen atom, the bond distances C11A-O4A and C11B-O4B are comparable to the bond distances C7A-O3A and C7B-O3B and are compatible with a double bond character for the carbonyl group.

Interestingly, a switch in the coordination of the amide occurs after chemical oxidation of dinuclear complex 1 at low temperature, and the complex obtained is a tetranuclear one constituted of two monoprotonated dinuclear units in the solid state. Because the final product obtained shows a protonation of the N atom of the terminal amide and consequently a change in the coordination of this amide, we investigated the direct effect of protonation on a solution of complex 1.

Solution Studies of the Protonated Species Obtained from Complex 1. Protonation of complex 1 by perchloric acid was followed by ¹H NMR and UV–vis spectroscopies and electrochemistry.

Table 3. Selected Bond Lengths and Angles for the Product(Complex 2) Recovered after Oxidation of Complex 1

bond lengths (Å) and angles (deg)						
Cu1A–O4A	1.975(6)	Cu2A-O1A	2.019(6)			
Cu1A-O1A	1.940(6)	Cu2A–O2A	1.909(6)			
Cu1A–O2A	1.920(6)	Cu2A-N1A	2.023(8)			
Cu1A-O1B	2.496(6)	Cu2A–N4A	2.006(8)			
Cu1A–N2A	1.891(8)	Cu2A–N5A	2.223(9)			
Cu1B-O1A	2.553(6)	Cu2B-O2A	2.779(7)			
Cu1B-O4B	1.980(7)	Cu2B-O1B	2.016(6)			
Cu1B-O1B	1.947(6)	Cu2B-O2B	1.915(7)			
Cu1B-O2B	1.916(6)	Cu2B-N1B	2.027(8)			
Cu1B-N2B	1.885(7)	Cu2B-N5B	2.242(8)			
C11A-O4A	1.243(11)	Cu2B-N4B	2.000(8)			
C11A-N3A	1.325(11)	C11B-O4B	1.257(12)			
C7A–O3A	1.238(12)	C11B-N3B	1.314(13)			
C7A–N2A	1.338(13)	C7B-O3B	1.268(12)			
		C7B-N2B	1.327(12)			
O4A-Cu1A-O2A	100.6(3)	O4B-Cu1B-O2B	100.3(3)			
O4A-Cu1A-N2A	84.5(3)	O4B-Cu1B-N2B	84.2(3)			
O1A-Cu1A-O2A	82.7(3)	O1B-Cu1B-O2B	83.1(3)			
O1A-Cu1A-N2A	92.7(3)	O1B-Cu1B-N2B	92.7(3)			
O1A-Cu2A-O2A	80.9(3)	O1B-Cu2B-O2B	81.2(3)			
O1A-Cu2A-N1A	93.2(3)	O1B-Cu2B-N1B	94.0(3)			
O1A-Cu2A-N5A	90.8(3)	O2B-Cu2B-N5B	101.0(3)			
O2A-Cu2A-N4A	102.1(3)	O2B-Cu2B-N4B	101.7(3)			
N1A-Cu2A-N4A	82.6(3)	N1B-Cu2B-N4B	82.3(3)			
Cu1A-O1A-Cu2A	94.2(3)	Cu1B-O1B-Cu2B	93.7(3)			
Cu1A-O2A-Cu2A	98.5(3)	Cu1B-O2B-Cu2B	98.1(3)			

¹*H* NMR Spectroscopy. Perchloric acid (1 M in acetonitrile) was added stepwise (from 0.25 to 1 equiv) to a solution of complex 1 in DMF- d_7 . After each addition, the ¹H NMR spectra were recorded at room temperature to follow the changes of the resonances of the protons (Figure 8). The ¹H NMR spectrum of 1 gradually changes upon the addition of acid; the intensities of some peaks decreased while new peaks appeared at the same time. Half an equivalent of acid conduces to the presence of two species in the same proportion, and the addition of 1 equiv of acid converts completely the first species into a new one. Analysis of the spectra indicates that these two

paramagnetic species possessed a hydroxido bridge characterized by the signals at -47 ppm and -42 ppm.

Electrochemistry. The redox behavior of complex 1 in the presence of acid was evaluated by cyclic voltammetry (Figure 9A). As for the NMR studies, aliquots of perchloric acid in acetonitrile (1 M) were added stepwise (from 0.25 to 1 equiv) to a solution of complex 1 (C = 0.65 mM) in DMF containing tetra-n-butyl ammonium perchlorate (TBAP) as the supporting electrolyte at T = 233 K. The addition of 1 equiv of acid produces a monoprotonated species with an anodic peak at E_{pa} (2) = 0.58 V at v = 0.1 V/s. The shift toward the anodic region of potential indicates that the new species formed is much harder to oxidize, and the irreversibility of this wave suggests that a chemical reaction occurs after the electron transfer. An interesting comparison could be made between the oxidation potential of this monoprotonated species generated by direct protonation and the new anodic wave detected at $E_{pa}(2) =$ 0.58 V vs Fc⁺/Fc during low-temperature electrolysis. These species display the same E_{pa} value, hence corroborating that complex 1⁺ evolves toward a monoprotonated species.

UV–vis Spectroscopy. Electronic absorption data were recorded during the titration of complex 1 with HClO₄ as shown in Figure 9B. Addition of acid results into the progressive shift of the LMCT transition at 460 nm to a shoulder around 410 nm. A ligand-centered transition at $\lambda = 315$ nm is also present as already observed for complex 1. An isosbestic point is observed at 393 nm, indicating that equilibrium between two species exists. We can suggest that complex 1 can be converted to a second dicopper(II) complex, as the d–d transition seemed to be only slightly affected. Even after the addition of 15 equiv of Et₃N, the original spectrum is not restored, confirming the relative stability of the monoprotonated complex.⁴⁸

Considering all the data collected in solution, we can suggest that the protonation site is the nitrogen of the terminal amide of the ligand. The detection of a ¹H NMR signal at $\delta = -42$ ppm confirms that the monoprotonated species also displays a hydroxido bridge between two copper centers. Complementary, the EPR silent spectrum (X band; 100 K) demonstrates that both copper ions are at the +II redox state, with an antiferromagnetic coupling. Moreover, the relatively high anodic potential (E_{pa} (2) = 0.58 V) in comparison to that



Figure 8. Variation of the chemical shift of the ¹H signals upon subsequent addition of $HClO_4$ to complex 1 in DMF- d_7 . The chemical shift of the proton of the hydroxido bridge of the complex is reported in the inset.



Figure 9. (A) Cyclic voltammograms of complex 1 after addition of 0 equiv (black), 0.25 equiv (orange), 0.5 equiv (red), 0.75 equiv (purple), and 1 equiv (blue) of a solution of HClO₄. Conditions: 0.65 mM solution of complex 1 in DMF, 0.1 M TBAP, T = 233 K. (B) UV–vis spectra of complex 1 before (black) and after addition of 0.25 equiv (orange), 0.5 equiv (red), 0.75 equiv (purple), and 1 equiv (blue) of a solution of HClO₄.

obtained for complex 1 (E_{pa} (1) = 0.16 V) indicates that the generated complex is better stabilized as a consequence of a change of coordination of the terminal amide. The protonation of the nitrogen of the amide decreases the donating power of the ligand and leads to the stabilization of the resulting Cu^{II}Cu^{II} complex.

Theoretical Calculations. Theoretical calculations can help to identify the molecular structure of the monoprotonated species obtained from complex 1 in solution. A first hypothesis is to consider the dinuclear complex corresponding to one halfunit of the tetranuclear complex obtained in solid state. For this dinuclear system, theory predicts a standard potential equal to 0.84 V vs Fc⁺/Fc with a spin density localized on the phenoxido ligand. This computed value corroborates perfectly with those found for similar complexes²⁵ but is significantly different from the experimental data obtained for the final product after chemical oxidation of 1 (E_{pa} (2) = 0.58 V vs Fc⁺/ Fc). This suggests that the complex in solution is not the halfunit of the tetranuclear complex. Other structures have thus to be considered for the monoprotonated form in solution. We have, for example, considered a dinuclear complex derived from the tetranuclear species but with one DMF molecule coordinated in an axial position to the Cu1A or Cu1B atom. According to our calculations, this complex is monoelectronically oxidized at 0.67 V vs Fc⁺/Fc, a value close to that found experimentally. Here, the oxidation occurs on the phenoxido ligand, leading to a bis-Cu(II) phenoxyl species as previously found for the BPMP derivatives.

Isolation and Characterization of the Protonated Species Obtained from Complex 1. Interestingly, addition of 1 equiv of HClO₄ to a solution of complex 1 in DMF, followed by diffusion of ethyl acetate, resulted in obtaining blue crystals that were suitable for X-ray diffraction (Figure S15; Table S4). Complex 2 crystallizes as $[(Cu_2(LH)(\mu-OH))_2](ClO_4)_2$ ·DMF·EtOAc) (2(ClO₄)_2·DMF·EtOAc), with one molecule of DMF and one molecule of ethyl acetate associated. The perchlorate ions are not coordinated to the copper centers as it was already evidenced by the vibrations at 1083 and 621 cm⁻¹ in the IR spectrum (Figure S17).^{49,50} This structure clearly shows the protonation of the terminal amide and the switch in the coordination previously observed in the structure of complex 2(SbF₆)(NO₂)·solvate recovered after chemical oxidation of 1 (see above). The main geometric features are quite similar in both structures (selected bond lengths and angles are given in Table S4).

Solubilization in DMSO of the blue crystals of **2** allows the detection by ESI-MS of two peaks (Figure S16), one at m/z = 574.03 corresponding to the molecular cation $[Cu_2(LH)(\mu - OH)]^+$ with the correct isotopic distribution and a second one at m/z = 1248.92 corresponding to the molecular ion peak $[(Cu_2(LH)(\mu - OH))_2 + ClO_4]^+$ which indicates the presence of dinuclear and tetranuclear species, respectively. A possible partial dissociation of the tetranuclear unit can be envisioned in solution.⁵¹

In summary, the neutral dinuclear complex 1 was synthesized and the characterization of its mono-oxidized species 1⁺ was performed. EPR analysis of the one-electron oxidized transient species formed is consistent with the formation of a mixed-valent Cu^{II}Cu^{III} complex. The lack of NIR band and the observed EPR feature allow the assignment of this species to a class I mixed-valent species in the Robin-Day classification, meaning a localized mixed-valence complex possessing distinguishable Cu(II) and Cu(III) sites, even though bridged.⁴⁷ The DFT calculations predicted a spin density for 1⁺ localized on one copper which corroborates with our outcome. Moreover, a band at $\lambda_{max} = 386$ nm detected by cryo-spectroelectrochemistry was ascribed to a UV feature of the one-electron oxidized species 1^+ . Natural transition orbitals of the excited state of 1^+ provide a reasonable assignment of this band as a ligand-to-metal charge transfer essentially between the phenoxido ligand and the Cu^{III} ion. In addition, attempts to characterize to the mono-oxidized species 1⁺ by chemical oxidation at low temperature were unsuccessful, but interestingly crystals of the final product 2 obtained after chemical oxidation were isolated. Complex 2 is a tetranuclear complex in which a switch in the coordination of the amide has occurred. Because complex 2 has shown a protonation of the N atom of the terminal amide and consequently a change in the coordination of this amide, the direct protonation of complex 1 was studied. Characterization in solution suggests that the protonation site is indeed the N atom of the terminal amide. This assumption is substantiated by the isolation of crystals of this monoprotonated species in two dinuclear Cu^{II}Cu^{II} units associated in a tetranuclear entity similar to the one obtained by chemical oxidation of complex 1. The different redox and proton transfer proposed to explain the presented studies are

Scheme 2. Proposed Pathways for the Monoelectronic Oxidation and Protonation of Complex 1



depicted in Scheme 2. Interestingly, the transient $Cu^{II}Cu^{III}$ phenoxido-hydroxido complex 1^+ evolves slowly at low temperature toward the tetranuclear complex 2, through the probable formation of a dinuclear bis-Cu(II) protonated species (alternatively detected by mass spectrometry). Strictly, this reaction involves the gain of either one hydrogen atom (HAT mechanism), or one proton and one electron (PCET mechanism), by the mixed-valent species.

CONCLUSIONS

A novel unsymmetrical ligand based on a phenoxido spacer has enabled obtaining a dissymmetric dicopper complex in which the two copper centers possess different coordination environments. On one side, the ligand offers a square planar and a strongly anionic environment which has allowed an oxidation centered on the metal supported by cryo-spectroelectrochemistry, EPR spectroscopy, and DFT calculations. This strategy has allowed the oxidation process to be directed on the metal center rather than on the ligand site which underlines that, even with a redox non-innocent spacer as the phenoxido, it is possible to obtain metal ion oxidation at lower potential value than that of the ligand. The low redox potential of this system makes it a good candidate for reactivity toward C-H activation. However, the mixed-valent species formed conduces to the formation of a new tetranuclear complex with a protonated ligand which coordinates the metal center by the O atom of the terminal amide. Although the ligand seems to be perfect in theory to stabilize high-valent copper, the basicity of the ligand associated with its close proximity of the oxidized metal center induces the rapid reactivity of this mixed-valent species. Nevertheless, this study shows that the geometry and a fine-tuning of the electronic properties of the ligand are important for controlling the locus of the oxidation. We are currently working on the ligand rigidity to avoid any switch in the coordination around the metal center and subsequent tetranuclear formation.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.8b02127.

NMR spectra and IR spectrum of H_3L ; IR spectrum, UV/vis spectrum, NMR spectra, mass spectrum, and electrochemical measurements of complex 1; crystallographic data for 1·DMF, $2(SbF_6)(NO_2)$ ·solvate, and $2(ClO_4)_2$ ·DMF·EtOAc; determination of the number of electrons for the oxidation of 1; main computed geometric parameters for 1, $1a^+$, and $1b^+$; crystal structure of compound $2(ClO_4)_2$ ·DMF·EtOAc; selected bond lengths and angles for compound $2(ClO_4)_2$ ·DMF·EtOAc; mass spectrum of complex $2(ClO_4)_2$ ·DMF·EtOAc; mass spectrum of the complex $2(ClO_4)_2$ ·DMF·EtOAc; IR spectrum of the complex $2(ClO_4)_2$ ·DMF·EtOAc; in solid phase (PDF)

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Accession Codes

CCDC 1578061–1578063 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The authors thank the French research agency for financial support ANR-13-BSO7-0018. This work has been carried out in the framework of COST action CM1305 (ECOSTBIO) and Labex ARCANE (ANR-11-LABX-0003-01). The authors wish to acknowledge the support from the ICMG Chemistry Nanobio platform for computer facilities, NMR and ESI-MS analysis, and X-ray characterizations. The authors acknowledge the ESRF for the allocation of beam time.

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