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## **Supporting Information**

## Ligand mediated dioxygen activation by mononuclear copper(II) complexes: A combined experimental and theoretical study

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## Experimental

*Physical Techniques*. FT-IR transmission spectra of the compounds, in KBr pellets, were acquired using a JASCO-460 model spectrophotometer. The purity of the ligands was confirmed by NMR spectroscopy. The samples were prepared from purified organic molecules in CDCl<sub>3</sub> at room temperature immediately prior to NMR spectrometric measurements. NMR spectra were recorded on a Bruker Avance 300 spectrometer at 300 MHz for <sup>1</sup>H. A 30°-pulse width was applied, and the spectra were acquired using 3000 Hz spectral window, and 1 s relaxation delay.

*UV-vis Spectroscopy*. The UV-vis measurements of the copper(II) compounds 1·2H<sub>2</sub>O, 2·CH<sub>3</sub>OH, 3 and 4 were recorded on a Photonics UV-vis spectrophotometer Model 400, equipped with a CCD array, operating in the range 250 to 1000 nm. Single crystals of 1or 2·CH<sub>3</sub>OH were dissolved in CH<sub>3</sub>OH or CH<sub>3</sub>CN and their concentration was in the range 1.0 x 10<sup>-5</sup> - 2.0 x 10<sup>-3</sup> M. The extinction coefficients of the peaks were calculated from the spectra and used to calculate the concentration of the copper(II) compounds during their reaction with the atmospheric O<sub>2</sub>. The UV-vis spectra were recorded *vs* time, at time intervals of 10 min in the first hour and then 30 min. The pseudo first order  $k_{int}$  reaction was calculated from the slope of the graph of the initial reaction rates at t = 0 *vs.* the complex concentration.

*X-ray Structure Analysis.* Details of crystallographic and experimental data for **1**, **2**·CH<sub>3</sub>OH, **3** and **4** are depicted in Table S1. X-ray diffraction data of single crystals of the copper(II) compounds were collected by means of a Xcalibur Oxford diffractometer equipped with a Sapphire 3 CCD detector and a 4-cycle Kappa geometry goniometer, using enhanced Mo  $K\alpha$  ( $\lambda = 0.71073$  Å) X-ray source and graphite radiation monochromator. Analytical absorption correction was applied using CrysAlis RED software. CrysAlis CCD and CrysAlis RED softwares were used for data collection and data reduction/cell refinement respectively. The structure of the copper (II) compounds was solved by direct methods and refined by fullmatrix least-squares techniques on  $F^2$  by using SHELXS-97.<sup>1, 2</sup> Special computing molecular graphics incorporated in the WinGX 3.2 interface were used.<sup>3</sup> All the non-H atoms were anisotropically refined. The positions of hydrogen atoms in all structures were calculated from stereochemical considerations and kept fixed isotropic during refinement or found in DF map and refined with isotropic thermal parameters.

*EPR spectroscopy.* The c. w. X-band EPR spectra of the copper(II) compounds  $1.2H_2O$ , 2·CH<sub>3</sub>OH, 3 and 4 in CH<sub>3</sub>CN and MeOH solutions at 130 K were measured on an ELEXSYS E500 Bruker spectrometer at resonance frequency ~9.5 GHz and modulation frequency 100 MHz. The resonance frequency was accurately measured with solid DPPH (g = 2.0036). The samples were prepared either with dissolution of the crystalline solid of the copper(II) compounds or by dissolving equimolar quantities of the ligands Hcapca or H<sub>2</sub>capcah and Cu<sup>II</sup>(CH<sub>3</sub>COO)<sub>2</sub>·H<sub>2</sub>O or Cu<sup>II</sup>Cl<sub>2</sub>·2H<sub>2</sub>O. The concentration of the copper (II) compounds was in the range 0.10-0.2 mM. The spectra of the solutions were acquired immediately after dissolution of the copper (II) species (t = 0 s) and at various time periods up to 3 weeks. The spectra were simulated using the software EasySpin 5.0.0.<sup>4</sup>

*ESI experimental.* (All MS data was collected using a Q-trap, time-of-flight MS (Maxis Impact MS) instrument supplied by Bruker Daltonics Ltd. The detector was a time-of-flight, micro-channel plate detector and all data was processed using the Bruker Daltonics Data Analysis 4.1 software, whilst simulated isotope patterns were investigated using Bruker Isotope Pattern software and Molecular Weight Calculator 6.45. The calibration solution used was Agilent ES tuning mix solution, Recorder No. G2421A, enabling calibration between approximately 100 m/z and 3000 m/z. This

solution was diluted 60:1 with MeCN. Samples were dissolved in MeOH and introduced into the MS *via* direct injection at 180  $\mu$ L h<sup>-1</sup>. The ion polarity for all MS scans recorded was negative, at 180 °C, with the voltage of the capillary tip set at 4000 V, end plate offset at –500 V, funnel 1 RF at 300 Vpp and funnel 2 RF at 400 Vpp.

*Computational Details.* All calculations were performed using the Gaussian09, D.01 program suite.<sup>5</sup> The geometries and thermal corrections for all stationary points along the reaction coordinate are computed with the Perdew, Burke and Ernzerhof<sup>6, 7</sup> of hybrid density functional denoted as PBE0 (also called PBE1PBE) as implemented in the Gaussian09 program suite. For the geometry optimizations we have used the Def2-TZVP basis set.<sup>8</sup> Hereafter the method used in DFT calculations is abbreviated as PBE0/Def2-TZVP. Frequency calculations were also performed at the same level of theory to identify whether the stationary point is a local minimum or a transition state. The transition states were confirmed by IRC calculations and each had only one imaginary frequency. The natural bond orbital (NBO) population analysis was performed using Weinhold's methodology as implemented in the NBO 6.0 software.<sup>9</sup> All calculations were performed in vacuum and in solution (CH<sub>2</sub>Cl<sub>2</sub> solvent) employing the Polarizable Continuum Model (PCM) using the integral equation formalism variant (IEFPCM) being the default self-consistent reaction field (SCRF) method.<sup>10</sup>

Infrared Spectra: Assignments of some diagnostic bands for the three ligands and their copper(II) complexes are given in Table S2. Differences between the spectra of H<sub>2</sub>capcah, Hcapca, Hmcapca and their corresponding complexes are readily noticeable. The medium-intesity bands at 3283 and 3282 cm<sup>-1</sup> in the spectra of Hcapca and Hmcapca respectively were assigned to the N-H stretching vibration, v(NH), of the secondary amide bond.<sup>11</sup> The IR spectrum of H<sub>2</sub>capcah exhibits two v(NH) at 3333 and 3055 cm<sup>-1</sup>, in accordance with the presence of two different N-H bonds (secondary amide, secondary amine) in its structure. The  $v(NH)_{amide}$  band is absent from the spectra of the complexes as expected from the stoichiometry. The amide deprotonation of the ligand in compound  $1.2H_2O$  results in the appearance of only one v(NH) [at 3205 cm<sup>-1</sup>] band in its IR spectrum attributable to the secondary amine stretch; this band has also v(OH) character from the lattice H<sub>2</sub>O molecules. In the spectra of all the complexes, the amide II and III bands [that are present in the spectra of the free ligands and are due to the coupling of the  $v(CN)_{amide}$  and  $\delta(NH)_{amide}$ modes] are replaced by a strong band in the 1383-1402cm<sup>-1</sup> region. This replacement might be expected as the removal of the amide proton produces a pure C-N stretch. The amide I band [ $\nu$ (C=O)] appears as a very strong band at 1663 and 1686 cm<sup>-1</sup> in the spectra of H<sub>2</sub>capcah and Hcapca/Hmcapca, respectively. This band appears at lower wavenumbers in the spectra of the complexes (1614-1637 cm<sup>-1</sup>); this shift can be explained by a decrease of the carbonyl double bond character due to a considerable degree of charge delocalization upon amide deprotonation and Ncoordination.

The band at ~620 cm<sup>-1</sup> in the spectra of the free ligands, attributable to the inplane deformation of the 2-pyridyl ring [ $\delta$ (py)], shifts to higher frequencies in the spectra of the copper(II) complexes. This shift has been interpreted<sup>12</sup> in terms of the

2-pyridyl N-coordination of Hcapcah<sup>-</sup> and capca<sup>-</sup>/mcapca<sup>-</sup>. The sharp band at 1590-1610 cm<sup>-1</sup> in the spectra of the complexes is due to an aromatic stretch;<sup>13</sup> in the spectra of  $2 \cdot CH_3OH$ , 3 and 4, this band should also have a v(C=N) character from the imine linkage. The far-IR spectra of 1·H<sub>2</sub>O and 2·CH<sub>3</sub>OH and 3 exhibit a distinct band at 359 (1·H<sub>2</sub>O), 268 cm<sup>-1</sup> (2·CH<sub>3</sub>OH) and 306 cm<sup>-1</sup> which is assigned to the stretching vibration of the terminal Cu<sup>II</sup>-Cl bonds. In the spectrum of 4, the bands at 1246 and 962 cm<sup>-1</sup> are tentatively assigned<sup>14</sup> to the  $v_{as}(NO_2)$  and  $v_s(NO_2)$  modes of the ligand pipyaz<sup>2-</sup>, respectively; the frequencies of these bands are indicative of the low N-O double bond character. There should be a delocalization of the six available  $\pi$ electrons over the -CHNO<sub>2</sub> skeleton which results in essentially a double bond for the carbon-nitrogen link almost single N-O bonds. and two,



**Fig. S1** MS of the oxidation of 1, A) a methanol solution of 1 at t=0 s, B) a methanol solution of 1 at t=24 h and C) a methanol solution of 1 and 1 equivalent of Et<sub>3</sub>N at t=0 s.



Fig. S2 ESI-MS of the system  $Cu^{II}Cl_2H_2O/Hmcapca$  (1:1 molar ratio) in methyl alcohol at 0, 6 and 24 hours after mixing  $Cu^{II}Cl_2H_2O$  and Hmcapca.



**Fig. S3** Selected structural parameters, natural atomic charges and Frontier Molecular Orbitals (FMOs) of  $[Cu(capca)]^+$  complex, the FMOs of dioxygen and  $[PyCH(NO_2)]^-$  nucleophile and the 3D plots of the spin density (isosurface = 0.002) of  $[Cu(capca)]^+$  and dioxygen(triplet state) calculated at the PBE0/def2-TZVP level in methanol solution.

parameters	<b>1</b> ·2H <sub>2</sub> O	<b>2</b> •CH <sub>3</sub> OH	3	4				
Empirical formula	C <sub>18</sub> H <sub>15</sub> ClCuN <sub>4</sub> O	$C_{19}H_{17}ClCuN_4O_2$	C <sub>19</sub> H <sub>15</sub> ClCuN <sub>4</sub> O	$C_{19}H_{13}CuN_5O_3$				
Formula weight	402.33	432.36	414.34	422.88				
Temperature	150(2)	100(2) K	150(2)	100(2) K				
Wavelength	0.71073 Å	0.71073 Å	0.71073 Å	0.71073 Å				
Crystsyst	Monoclinic	Triclinic	Monoclinic	Triclinic				
Space group	P 21/c	<i>P</i> -1	P 21/n	<i>P</i> -1				
$a(\text{\AA})$	11.1506(5)	8.5866(7)	11.418(5)	9.3955(7)				
b(Å)	13.6960(6)	8.9466(7)	14.822(7)	9.9665(8)				
$c(\text{\AA})$	11.6476(5)	12.3484(8)	11.554(5)	10.3694(8)				
$\Box$ (deg)	90	85.996(6)	90	114.702(7)				
$\Box$ (deg)	112.259(2)	73.744(6)	118.160(5)	98.054(6)				
$\Box$ (deg)	90	75.759(7)	90	106.554(7)				
Vol.(Å <sup>3</sup> )	1646.25(13)	882.70(12)	1723.9(14)	807.26(12)				
Ζ	4	2	4	2				
$\Box_{calcd}$ (Mg/m <sup>3</sup> )	1.623	1.627	1.596	1.740				
Abscoeff (mm <sup>-1</sup> ) arrange for data collection (deg) Index ranges	1.503	1.412	1.438	1.388				
	1.97 to 27.12	2.909 to 28.900	2.067 to 26.539	3.184 to 28.951				
	-14<=h<=14, - 17<=k<=17, - 12<=l<=14	-11<=h<=11, - 11<=k<=11, - 16<=l<=15	-14<=h<=14, - 18<=k<=18, - 14<=1<=14	-12<=h<=12, - 11<=k<=13, - 11<=l<=13				
Collected	14523	7159	20832	5500				
Unique	3631	4054	3590	3661				
Rint	0.0253	0.0524	0.0547	0.0222				
ers	3631 / 0 / 226	4054 / 2 / 264	3590 / 0 / 236	3661 / 0 / 257				
GOF on $F^2$	1.058	1.078	1.014	1.047				
$Max/min\Box p \text{ (eÅ}^{-3}\text{)}$	0.860 and -0.474	1.962 and -1.026	0.389 and -0.385	0.677 and -0.493				
Final <i>R</i> indies ( <i>R</i> , w <i>R</i> ) $[I \ge 2\Box(I)]$	0.0269, 0.0727	0.0586, 0.1436	0.0316, 0.0624	0.0380, 0.0862				
<i>R</i> , w <i>R</i> (all data)	0.0306, 0.0752	0.0725, 0.1631	0.0478, 0.0680	0.0471, 0.0922				
${}^{a}[R = \Sigma  F_{o}  -  F_{c}  /\Sigma F_{o} , wR = [\Sigma w( F_{o} ^{2} -  F_{c} ^{2})/\Sigma w F_{o} ^{2}]^{1/2}, \text{GOF} = [\Sigma [w(F_{o}^{2} - F_{c}^{2})^{2}]/(n-p)]^{1/2}, w = 1/[\sigma^{2}(F_{o}^{2})/\Sigma w F_{o} ^{2}]^{1/2}, w = 1$								

**Table S1** Crystallographic and experimental data for  $1, 2 \cdot CH_3OH, 3$  and  $4^a$ 

+  $(aP)^2 + bP$ , where  $P = (F_0^2 + 2F_c^2)/3$ .

	v (NH)	$v (CO)^a$	amide II <sup>b</sup>	$v(CN)_{amide}$	amide III <sup>b</sup>	$\delta(\mathrm{py})^c$
H <sub>2</sub> capcah	3333 (s), 3055 (w)	1663 (vs)	1520 (vs)		1272 (w)	621 (m)
<b>1</b> ·2H <sub>2</sub> O	3205 (w) <sup>d</sup>	1622 (s)		1393 (s)		652 (m)
Нсарса	3283 (m)	1686 (vs)	1533 (vs)		1277(m)	619 (m)
<b>2</b> ·CH <sub>3</sub> OH		1630 (vs)		1389 (vs)		650 (w)
Нтсарса	3285 (w)	1686 (vs)	1529 (vs)		1299(m)	621 (m)
3		1626 (vs)		1390 (s)		644 (w)
4		1628 (s)		1387 (s)		645 (w)

Table S2 Diagnostic infrared bands [cm<sup>-1</sup>] of the ligands and their copper(II) compounds

<sup>*a*</sup>In secondary amides the v(C=O) vibration is called amide I. <sup>*b*</sup>In secondary amides, these bands arise from coupled v(CN) and  $\delta(NH)$  modes. <sup>*c*</sup>In-plane pyridine ring deformation. <sup>*d*</sup>This band should also have a v(OH) component.

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