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# Introduction

Dioxygen activation and transition-metal-catalyzed oxidation processes play a crucial role in many biological systems,<sup>1–12</sup> environmental chemistry,<sup>13</sup> medicinal chemistry<sup>14</sup> and industrial applications.<sup>15–17</sup> Copper monooxygenases and copper dioxygenases are the best known copper proteins that bind and/or activate molecular oxygen in many biological processes.<sup>18–20</sup> The copper monooxygenases are mainly involved in hydrocarbon oxidations such as tyrosinase (Tyr),<sup>20</sup> catechol oxidase (CO),<sup>21</sup> dopamine  $\beta$ -monooxygenase, D $\beta$ M,<sup>22</sup>

# Air oxygenation chemistry of 4-TBC catalyzed by chloro bridged dinuclear copper(II) complexes of pyrazole based tridentate ligands: synthesis, structure, magnetic and computational studies†

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Four dinuclear bis( $\mu$ -Cl) bridged copper( $\parallel$ ) complexes,  $[Cu_2(\mu-Cl)_2(L^X)_2](ClO_4)_2$  ( $L^X = N,N$ -bis[(3,5-dimethylpyrazole-1-yl)-methyl]benzylamine with X = H(1), OMe(2), Me(3) and Cl(4)), have been synthesized and characterized by the single crystal X-ray diffraction method. In these complexes, each copper( $\parallel$ ) center is penta-coordinated with square-pyramidal geometry. In addition to the tridentate  $L^X$  ligand, a chloride ion occupies the last position of the square plane. This chloride ion is also bonded to the neighboring Cu( $\parallel$ ) site in its axial position forming an *SP*-I dinuclear Cu( $\parallel$ ) unit that exhibits small intramolecular ferromagnetic interactions and supported by DFT calculations. The complexes **1–3** exhibit methylmonooxygenase (*p*MMO) behaviour and oxidise 4-*tert*-butylcatechol (4-TBCH<sub>2</sub>) with molecular oxygen in MeOH or MeCN to 4-*tert*-butyl-benzoquinone (4-TBQ), 5-methoxy-4-*tert*-butyl-benzoquinone (5-MeO-4-TBQ) as the major products along with 6,6'-Bu<sup>t</sup>-biphenyl-3,4,3',4'-tetraol and others as minor products. These are further confirmed by ESI- and FAB-mass analyses. A tentative catalytic cycle has been framed based on the mass spectral analysis of the products and DFT calculations on individual intermediates that are energetically feasible.

> peptidylglycine  $\alpha$ -amidating monooxygenase (PHM),<sup>23,24</sup> methane monooxygenase  $(p-MMO)^{25-27}$  etc. In these oxidation processes, the copper(II) metal ions in mono- or dinuclear active cores are reduced into copper(1) by an external reductant prior to binding and activation of molecular oxygen. Monooxygenases play a crucial role in the activation by inserting singlet oxygen into relatively strong C-H bonds. The products from these reactions are vital for the organisms in which these proteins are formed. On the other hand, in copper dioxygenase systems, such as quercetin 2,3-dioxygenase (2,3-QD), the reaction is believed to occur through substrate activation by an inner-sphere coordination of the deprotonated polyhydroxylated organic substrate (RO<sup>-</sup>). The electron transfer to copper(II) initially occurs to generate copper(1) and an organic radical intermediate (RO<sup>•</sup>) of the substrate.<sup>28</sup> The generated RO<sup>•</sup>/ copper(I) pair readily reacts with  $O_2$  to promote the substrate oxygenation reaction.

> Different possible active intermediates in mononuclear copper monooxygenases are  $Cu^{II}$ -O-O (end-on superoxo),<sup>29</sup>  $Cu^{II}$ -O-O-H (hydroperoxo)<sup>30</sup> and  $Cu^{III}$ =O (higher valent oxo) species (Fig. 1).<sup>29-32</sup>

Therefore, independent synthesis of small molecules containing these motifs and examination of their reactivities

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**Fig. 1** Schematic presentation of the proposed binding sites of type 2  $Cu^{2+}$  in *p*MMO from ref. 36 and representative  $[Cu(L^H)CI]^+$  complex in solution of the present study.



should provide some insights into how these monooxygenases work and should help to develop bio-inspired oxidation catalysts. This type of investigation has been less developed in model systems involving mononuclear copper( $\pi$ ) complexes in comparison to the comprehensive copper(i) dioxygen studies.

In dihalogen-bridged copper complexes, metal centers usually adopt a tetra- or penta-coordinated geometry with different types of terminal/capping ligands leading to a wide variety of ferro- or antiferro-magnetic interactions. For five coordinated metal centers, three different geometries of dihalogen-bridged complexes have been experimentally observed (Scheme 1): (i) SP-I, for which the two shared halogens occupy at the same time the axial position of the first  $Cu(\pi)$  site and one of the four equatorial positions of the second  $Cu(\pi)$  center; this configuration usually leads to small ferromagnetic or antiferromagnetic coupling; (ii) SP-II, for which the two halogens form a sharing edge of both Cu(II) basal planes leading to quasi-coplanar pyramidal bases showing different magnetic behaviors that depend strongly on the nature of co-ligands; and (iii) SP-III, for which the first halogen is shared between the two Cu(II) sites in their axial positions while the second one occupies simultaneously equatorial positions for both metal ions. This arrangement, that is relatively rare, usually leads to almost perpendicular Cu(II) basal planes and ferromagnetic coupling.33-35

In this work, we report four dinuclear  $[Cu_2(\mu-Cl)_2(L^X)_2]^{2+}$ complexes of the *SP*-I type that exhibit weak intramolecular ferromagnetic interactions and also act as a copper monooxygenases model. The observed EPR spectrum for the type 2 center in the native *p*MMO consisted of  $g_{\parallel} = 2.24$  with  $A_{\parallel}(Cu) =$ 185 G and  $g_{\perp} = 2.04^{36}$  which are comparable to our system (*vide infra*). The combined CW and ESEEM data for pMMO indicate that the coordination environment comprises four nitrogen atoms coordinated to the Cu center and that three or four of these nitrogens are histidine imidazoles. In this respect the mononuclear species of our systems closely resembles structurally and spectroscopically the active site of *p*MMO.

# **Experimental section**

#### Materials and reagents

The starting materials for the synthesis of the ligands like acetylacetone (Merck, India), hydrazine hydrate (Rankem), formalin (Merck, India), benzyl amine derivatives (Aldrich),  $Na_2SO_4$  (Merck, India) are of reagent grade and used as received. Copper(II) perchlorate hexahydrate and copper(II) chloride dihydrate (Loba Chemie, India) are used for the preparation of complexes. Tetrabutylammonium perchlorate was purchased from Aldrich. Solvents like methanol, ethanol, chloroform, diethyl ether, acetonitrile (Merck, India) were of reagent grade and dried before use.

Synthesis of the bis(pyrazoline) derivative of tripodal ligands  $(L^{X})$ : 3,5-Dimethylpyrazole and 3,5-dimethyl-1-hydroxymethylpyrazole were prepared by following the literature procedure.<sup>37</sup>

Preparation of ligands ( $L^{X}$ , X = Cl, H, Me and OMe): All ligands ( $L^{X}$ ) were synthesized by following the literature procedure.<sup>37</sup> A solution of 12 mmol of the corresponding amine and 24 mmol of 3,5-dimethyl-1-hydroxymethyl pyrazole in 50 ml acetonitrile were stirred in a stoppered vessel at room temperature for 24 hours. The water produced during the reaction was removed by drying over anhydrous Na<sub>2</sub>SO<sub>4</sub>. After filtration and evaporation under reduced pressure, an oily substance was obtained. A white crystalline product was isolated after dissolution of the oily material in diethyl ether and cooling in the refrigerator. The white crystals were harvested by filtration and dried in air.

**L<sup>H</sup>:** Yield 60%. *Ana. Cal.* value for molecular formula  $C_{19}H_{25}N_5$ : C, 66.86; H, 7.92; N, 19.62; *Found* C, 65.26; H, 7.26; N, 20.5%.<sup>1</sup>H NMR(CDCl<sub>3</sub>, δ, ppm): 1.99 (6H,s); 2.17 (6H,s); 3.69 (2H,s); 4.93 (4H,s); 5.42 (2H,s); 7.1–7.3 (5H,m). <sup>13</sup>C NMR(CDCl<sub>3</sub>, δ, ppm): 149.4 (C3); 140.9 (C5); 105.4 (C4); 127.3 (C13); 135.6 (C10); 128.5 (C11, 12, 14, 15); 61.4 (C8); 55.7 (C6); 18.0 (C7); 11.2 (C6).

**L**<sup>OMe</sup>: Yield 65%. *Ana. Cal.* value for molecular formula  $C_{20}H_{27}N_5O$ : C, 67.90; H, 7.64; N, 19.80; *Found* C, 68.16; H, 7.23; N, 20.06%.<sup>1</sup>H NMR(CDCl<sub>3</sub>, δ, ppm): 1.98 (6H,s); 2.19 (6H,s); 3.62 (2H,s); 3.76 (2H,s); 4.88 (4H,s); 5.77 (2H,s); 6.78–7.09 (4H,d). <sup>13</sup>C NMR(CDCl<sub>3</sub>, δ, ppm): 147.52 (C3); 139.91 (C5); 160.25 (C13); 129.9 (C11, 15); 127.9 (C10); 113.69 (C12, 14); 105.64 (C4); 64.74 (C8); 55.24 (C16); 51.98 (C9); 13.50 (C7); 10.67 (C6); 55.24 (C16, OMe).

**L**<sup>Me</sup>: Yield 60%. *Ana. Cal.* value for molecular formula  $C_{20}H_{27}N_5$ : C, 71.21; H, 8.01; N, 20.70; *Found* C, 70.15; H, 7.49; N, 20.80. <sup>1</sup>H NMR(CDCl<sub>3</sub>,  $\delta$ , ppm): L<sup>Me</sup> (X = Me) 1.99 (6H,s); 2.18 (3H,s); 3.63 (2H,s); 4.90 (4H,s); 5.77 (2H,s); 7.06 (4H,q). <sup>13</sup>C NMR(CDCl<sub>3</sub>,  $\delta$ , ppm): 147.52 (C3); 139.91 (C5); 136.78 (C13); 134.96 (C10); 128.98 (C11, 12, 14, 15); 105.63 (C4); 64.74 (C8); 52.22 (C9); 13.50 (C7); 10.67 (C6); 21.08 (C16, Me).



L<sup>Cl</sup>: Yield 55%. Ana. Cal. value for molecular formula C<sub>19</sub>H<sub>24</sub>N<sub>5</sub>Cl: C, 63.77; H, 6.71; N, 19.58; Found C, 64.01; H, 6.89; N, 19.40%. <sup>1</sup>H NMR(CDCl<sub>3</sub>, δ, ppm): 2.32 (6H,s); 3.62 (6H,s); 4.80 (4H,s); 5.82 (2H,s), 7.78 (4H,s). <sup>13</sup>C NMR(CDCl<sub>3</sub>, δ, ppm): 148.32 (C3); 139.92 (C5); 132.8 (C13); 129.9 (C11, 15); 128.02 (C12, 14); 106.04 (C4); 64.84 (C8); 55.24 (C6); 13.50 (C7); 11.2 (C6).

Preparation of the  $[Cu(L^X)Cl]_2(ClO_4)_2$  complexes: 0.25 mmol of Cu(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O was solubilized in MeOH (15 ml) and stirred for a few minutes before the addition of 0.25 mmol of CuCl<sub>2</sub>·2H<sub>2</sub>O. The corresponding L<sup>X</sup> ligand was added to the light green copper solution that turned dark green. After six hours of stirring, the solution was filtered and kept in a refrigerator. After two to three days, green crystals formed that were isolated by filtration and air dried.  $[{Cu(L^{H})Cl}]_{2}(ClO_{4})_{2}$ (1): Yield 60%, Anal. Calcd for C<sub>38</sub>H<sub>50</sub>Cl<sub>4</sub>Cu<sub>2</sub>N<sub>10</sub>O<sub>8</sub>: C, 43.69; H, 4.79; N, 13.41. Found: C, 43.60; H, 4.78; N, 13.63. [{Cu  $(L^{OMe})$ -Cl}]<sub>2</sub>(ClO<sub>4</sub>)<sub>2</sub> (2): Yield 70%, Anal. Calcd for C<sub>40</sub>H<sub>54</sub>Cl<sub>4</sub>-Cu<sub>2</sub>N<sub>10</sub>O<sub>10</sub>: C, 43.52; H, 4.89; N, 12.69. Found: C, 43.17; H, 4.75; N, 12.33. [{Cu(L<sup>Me</sup>)Cl}]<sub>2</sub>(ClO<sub>4</sub>)<sub>2</sub> (3): Yield 64%, Anal. Calcd for C40H54Cl4Cu2N10O8: C, 44.82; H, 5.08; N, 13.07. Found: C, 44.69; H, 4.99; N, 12.57.  $[{Cu(L^{Cl})Cl}]_2(ClO_4)_2$  (4): Yield 54%, Anal. Calcd for C<sub>38</sub>H<sub>46</sub>Cl<sub>6</sub>Cu<sub>2</sub>N<sub>10</sub>O<sub>8</sub>: C, 41.09; H, 4.31; N, 12.61. Found: C, 40.77; H, 4.18; N, 12.27.

# **Physical measurements**

Elemental analyses were carried out using a Perkin-Elmer 240 elemental analyzer. Infrared spectra (400-4000 cm<sup>-1</sup>) were

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recorded from KBr pellets on a Nickolet Magna IR 750 series-II FTIR spectro-photometer. <sup>1</sup>H and <sup>13</sup>C NMR were recorded in CDCl<sub>3</sub> on a Bruker 300 MHz NMR Spectrophotometer using tetramethylsilane ( $\delta = 0$ ) as an internal standard. Electronic spectra were recorded on an Agilent-8453 diode array UV-vis spectrophotometer. Electrochemical measurements were carried out using a computer-controlled AUTOLAB (model 263A VERSASTAT) electrochemical instrument with a platinum tip as the working electrode.

#### Crystallography

Single crystal X-ray data of 1-4 were collected at room temperature on a Bruker SMART APEX-II CCD diffractometer using graphite monochromated MoK<sub> $\alpha$ </sub> radiation ( $\lambda$  = 0.71073 Å). Data integration and reductions were processed with SAINT+ software.<sup>38</sup> Structures were solved by the direct method and then refined on  $F^2$  by the full matrix least squares technique with SHELX-97 software.<sup>39</sup> During the refinement of these structures some restraints were imposed, for example, Cl-O bond distances were fixed in space and in most cases oxygen atoms of perchlorate ions were refined considering the ISOR model. The crystallographic data for 1–4 are given in Table 1.

#### Magnetic measurements

The magnetic susceptibility measurements were carried out on an MPMS-XL Quantum Design SQUID magnetometer between 1.8 and 400 K for dc applied fields ranging from -7 to 7 T on polycrystalline samples of 1-4. ac susceptibilities were measured with an oscillating ac field of 3 Oe with frequencies

Table 1 Crystal data and structural	refinement parameters			
	CCDC 716786 (1)	CCDC 893810 (2)	CCDC 716784 (3)	CCDC 716785 (4)
Empirical formula	$C_{38}H_{50}Cl_4Cu_2N_{10}O_8$	$C_{42}H_{62}Cl_4Cu_2N_{10}O_{12}$	$C_{40}H_{54}Cl_4Cu_2N_{10}O_8$	$C_{38}H_{48}Cl_6Cu_2N_{10}O_8$
Formula weight	1043.76	1167.92	1071.83	1112.64
Temperature (K)	293(2)	293(2)	293(2)	293(2)
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Triclinic	Triclinic	Triclinic
Space group	$P2_1/c$ (No. 14)	<i>P</i> 1̄ (No. 2)	<i>P</i> 1̄ (No. 2)	<i>P</i> 1̄ (No. 2)
Unit cell dimensions (Å, °)	a = 8.427(15)	a = 9.4248(14)	a = 9.187(6)	a = 9.1275(12)
	b = 21.205(4)	b = 11.5255(17)	b = 10.264(6)	b = 10.1836(14)
	c = 12.694(2)	c = 12.6536(19)	c = 12.987(8)	c = 13.1067(18)
	$\alpha = 90.00(3)$	$\alpha = 85.280(8)$	$\alpha = 76.354(9)$	$\alpha = 75.730(2)$
	$\beta = 96.680(3)$	$\beta = 86.063(9)$	$\beta = 74.315(9)$	$\beta = 73.331(2)$
		$\gamma = 78.893(8)$	$\gamma = 89.607(9)$	$\gamma = 89.528(2)$
Volume (Å <sup>3</sup> )	2252.949(7)	1342.2(3)	1143.6(12)	1128.5(3)
Z	2	1	1	1
Density calcd ( $g \text{ cm}^{-3}$ )	1.539	1.445	1.556	1.637
Absorption coefficient (mm <sup>-1</sup> )	1.242	1.056	1.226	1.360
F(000)	1076	606	554	570
Crystal size (mm <sup>3</sup> )	$0.40 \times 0.43 \times 0.47$	0.20  imes 0.15  imes 0.12	$0.39 \times 0.42 \times 0.46$	$0.39 \times 0.42 \times 0.45$
$\theta$ range (°)	1.88 to 25.05	2.21 to 27.01	1.68 to 27.25	1.68 to 27.50
Limiting indices	$-10 \le h \le 10,$	$-12 \le h \le 12,$	$-11 \le h \le 12,$	$-11 \le h \le 12,$
	$-25 \le k \le 25,$	$-14 \le k \le 14,$	$-13 \le k \le 13,$	$-13 \le k \le 13,$
	$-16 \le l \le 14$	$-16 \le l \le 16$	$-16 \le l \le 16$	$-17 \leq l \leq 16$
Reflections collected	16 028	17 891	12 698	13 118
Independent reflections	3987 [R(int) = 0.035]	5858 [R(int) = 0.1090]	5190 [R(int) = 0.040]	5217 [R(int) = 0.013]
Data $[I > 2\sigma(I)]$ /parameters	3986/302	3874/326	3883/294	4701/293
Goodness-of-fit on $F^2$	1.041	1.032	0.909	0.695
Final <i>R</i> indices $[I > 2\sigma(I)]$	$R_1 = 0.0601, wR_2 = 0.1668$	$R_1 = 0.0936$ , w $R_2 = 0.2496$	$R_1 = 0.0623, wR_2 = 0.1715$	$R_1 = 0.0325, WR_2 = 0.1014$

 $w = 1/[\sigma^2 (F_0^2) + (0.1588P)^2 + 10.3950P]$ , where  $P = (F_0^2 + 2F_c^2)$ .

between 1 and 1500 Hz. It is worth noting that no out-of-phase ac susceptibility signal has been detected above 1.8 K. The magnetic data were corrected for the sample holder (plastic bag) and the diamagnetic contribution.

### **DFT calculations**

Geometries of the complexes  $[Cu(L^X)Cl]_2^{2+}$  (X = H(1), OMe(2), Me(3), Cl(4)) were fully optimized starting with the geometries obtained from single-crystal X-ray diffraction studies by DFT computations using the Gaussian 03 program<sup>40</sup> with the Becke three-parameter exchange and Lee-Yang-Parr correlation functional (B3LYP).<sup>41</sup> The LanL2DZ<sup>42</sup> basis functions and effective core potentials (ECP) were used for all atoms including copper. These basis functions were augmented with additional polarization functions of exponents: Cu ( $\zeta_f$  = 0.8), C ( $\zeta_d$  = 0.8), N ( $\zeta_d$  = 0.8), O ( $\zeta_d$  = 0.8), Cl ( $\zeta_d$  = 0.75). The nature of all stationary points was confirmed by harmonic vibrational frequency analysis. For all the four complexes, the ground state belongs to a triplet multiplicity. The exchange coupling constant (1) between the two magnetic Cu-centers of the chloro bridged Cu(II) dimers is calculated from the energy difference between the triplet (T) ground state and singlet (S) excited state energies as  $E_{\rm T} - E_{\rm S} = -2J$  of the complex using the Heisenberg-Dirac-van Vleck spin Hamiltonian. The broken-symmetry (BS) formalism proposed by Noodleman<sup>43</sup> within the framework of DFT has been found to be efficient in calculating the exchange coupling constant, J. The BS state is not the eigenstate of the spin Hamiltonian but an equal mixture of a singlet and triplet state which is obtained when magnetic orbitals are allowed to overlap in a self-consistent field (SCF) manner. The energy of the BS state is basically a specific weighted average of energies of the pure spin multiplets. The exchange coupling constant, *I*, for a binuclear system can be determined from the energies of the BS and the triplet states following the formula of Yamaguchi and coworkers:44

$$J = \frac{\left({}^{\rm DFT}E_{\rm BS} - {}^{\rm DFT}E_{\rm T}\right)}{\left\langle S^2 \right\rangle_{\rm T} - \left\langle S^2 \right\rangle_{\rm BS}} \tag{1}$$

where  $E_{\rm BS}$  and  $E_{\rm T}$  are the energies of the broken symmetry and triplet state, respectively.  $\langle S^2 \rangle_{\rm T}$  and  $\langle S^2 \rangle_{\rm BS}$  denote the square of the total spin for the triplet and BS state, respectively.

#### **Kinetic experiments**

All kinetic experiments were performed with an Agilent diodearray UV-VIS spectrophotometer under pseudo-first-order conditions, with the copper complexes as the minor component. The kinetic procedures involve the preparation of stock solutions of the complexes and the substrate 4-TBCH<sub>2</sub> at higher concentrations in pure MeCN. From these stock solutions, a set of 11–12 solutions of [4-TBCH<sub>2</sub>] = 1.0–50 mM were prepared. A 2 ml portion of each solution was pipetted out into a quartz cell and thermostated for 15 min at 25 °C by inserting into the shell holder which is attached to a peltier temperature controller system. 20 µl of a stock solution of the complex was added to the 4-TBCH<sub>2</sub> solution to achieve a 0.50 mM concentration of the complex. The formation of 3-methoxy-4-TBQ was monitored with time at a wavelength of 386 nm. The observed rate constants ( $k_i$ ) were extracted by a linear regression fit of the kinetic traces (initial rate method) for more than 3-half-lives. A weighted average of triplicate runs of each experiment indicates that the error limit falls well within ±5%.

# **Results and discussion**

# Synthesis, characterizations and structural description of complexes 1-4

The four complexes were synthesized in a similar synthetic approach. A 1:1 mixture of perchlorate and chloride salts of Cu(II) in methanol was allowed to react with a stoichiometric amount of functionalized N,N-bis[(3,5-dimethylpyrazole-1-yl)methyl]benzylamine ligands at room temperature for about six hours. Green crystals suitable for single-crystal X-ray diffraction studies were easily obtained in a couple of days by the slow evaporation technique at about 4 °C. The dicationic parts of the complexes 1-4 are shown in Fig. 2 and selected bond distances and angles are listed in Table 2. Complex 1 crystallizes in the monoclinic space group  $P2_1/c$  while the three other complexes adopt a triclinic space group P1. In all these compounds, the Cu(II) metal ions are the dichloro-bridged dinuclear units which are five-coordinated and adopt a distorted square-based pyramidal geometry. The L<sup>X</sup> ligands coordinate the Cu(II) centers by three nitrogen atoms (two from two pyrazole rings and one from the functionalized benzyl amine) that occupy three of the four Cu(II) equatorial positions. One chlorine atom completes the basal plane and is shared with the neighboring Cu(II) metal center in its single apical position. In the four compounds, the equatorial planes of the two copper sites in the dinuclear centrosymmetrical cation moiety are almost coplanar with the dihedral angle ~3.69°. The copper center lies perfectly in its [N<sub>3</sub>Cl] basal plane and is not displaced toward the axial chlorine atom as is often observed in square-pyramidal geometry. The distortion from ideal



Fig. 2 Ortep-type view of the four  $[Cu_2(\mu-Cl)_2(L^X)_2](ClO_4)_2$  (with X = H (1), OMe (2), Me(3) and Cl (4)) complexes. Thermal ellipsoids are at the 30% probability level.

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Table 2	Selected bond	distances and bon	d angles of	f complexes	1–4.	Values in square	brackets are	from DFT	calculations
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Complex 1		Com	plex 2	Com	plex 3	Com	plex 4
Cu1-Cl1	2.2397(14) [2.315]	Cu1-Cl1	2.228 (15) [2.315]	Cu1-Cl1	2.2329(14) [2.316]	Cu1-Cl1	2.2340(6) [2.317]
Cu1-N1	1.972(4) [2.166]	Cu1-N1	1.987(4) [2.040]	Cu1-N1	1.965(3) [2.011]	Cu1-N1	2.0822(18) [2.166]
Cu1-N11	1.977(4) [2.015]	Cu1-N3	2.083(4) [2.016]	Cu1-N3	1.986(3) [2.031]	Cu1-N3	1.9704(19) [2.018]
Cu1-N9	2.084(4) [2.034]	Cu1-N5	1.980(4) [2.160]	Cu1-N5	2.088(3) [2.166]	Cu1-N4	1.982(2) [2.044]
Cu1-Cl1_a	2.896(1) [2.858]	Cu1-Cl1_a	2.831(1) [2.878]	Cu1-Cl1_a	2.844(1) [2.878]	Cu1-Cl1_a	2.8301(7) [2.843]
Cu1…Cu1_a	3.542 [3.723]	Cu…Cu	3.449 [3.731]	Cu…Cu	3.526 [3.742]	Cu…Cu	3.522 [3.706]
N1-Cu1-Cl1	99.20(13) [92.3]	Cl1-Cu1-N1	98.29(15) [100]	Cl1-Cu1-N1	98.97(9) [100.7]	Cl1-Cu1-N1	178.86(5) [178.9]
N11-Cu1-Cl1	98.21(13) [91.8]	Cl1-Cu1-N3	176.52(10) [99.9]	Cl1-Cu1-N3	98.47(9) [99.2]	Cl1-Cu1-N3	99.02(6) [99.9]
N9-Cu1-Cl1	178.64(13) [178.3]	Cl1-Cu1-N5	98.51(14) [179.4]	Cl1-Cu1-N5	178.95(8) [178.5]	Cl1-Cu1-N4	98.53(6) [100.3]
Cl1-Cu1-Cl1_a	93.79(4) [88.6]	Cl1-Cu1-Cl1_a	94.92(5) [88.8]	Cl1-Cu1-Cl1_a	92.89(3) [88.5]	Cl1-Cu1-Cl1_a	92.70(2) [88.8]
N1-Cu1-N11	162.57(17) [159.3]	N1-Cu1-N3	81.93(17) [159.6]	N1-Cu1-N3	162.34(11) [159.5]	N1-Cu1-N3	81.88(8) [80.5]
N1-Cu1-N9	80.88(17) [79.4]	N1-Cu1-N5	162.04(2) [79.4]	N1-Cu1-N5	81.90(12) [79.0]	N1-Cu1-N4	80.53(8) [79.3]
Cl1Cu1-N1	90.58(8) [93.6]	Cl1_a-Cu1-N1	91.05(1) [92.6]	Cl1_a-Cu1-N1	91.81(9) [92.4]	Cl1_a-Cu1-N1	87.97(5) [92.2]
N11-Cu1-N9	81.69(10) [80.6]	N3-Cu1-N5	81.12(17) [80.6]	N3-Cu1-N5	80.63(12) [79.3]	N3-Cu1-N4	162.08(8) [159.2]
Cl1_a-Cu1-N11	89.24(8) [92.3]	Cl1_a-Cu1-N3	88.54(1) [91.8]	Cl1_a-Cu1-N3	90.00(8) [93.0]	Cl1_a-Cu1-N3	92.48(6) [93.1]
Cl1_a-Cu1-N5	8758 (8) [91.8]	Cl1_a-Cu1-N5	90.45(1) [91.0]	Cl1_a-Cu1-N5	87.65(8) [91.6]	Cl1_a-Cu1-N4	90.26(5) [92.7]
Cu1-Cl1_a-Cu1_a	86.21(4)[91.4]	Cu1-Cl1-Cu1_a	85.08(5)[91.2]	Cu1-Cl1-Cu1_a	87.11(3) [91.5]	Cu1-Cl1-Cu1_a	87.30(2) [91.2]

square pyramidal geometry estimated from Reedijk's  $\tau$  factor<sup>45</sup> ( $\tau = 0$  for a square pyramid, and  $\tau = 1$  for a trigonal bipyramid) for all four complexes was found to lie between 0.27 and 0.28. In the equatorial plane, the Cu-N<sub>amine</sub> (N<sub>amine</sub> = tertiary amine nitrogen) distance range 2.034-2.086 Å is slightly longer than the two other  $Cu-N_{PZ}$  ( $N_{PZ}$  = coordinated nitrogen atom of the pyrazole ring) distances that range between 1.967 and 1.998 Å. The axial Cu-Cl distance in the four complexes ranges as 2.830-2.896 Å that is considerably longer than the basal Cu-Cl distance 2.228-2.239 Å. However, the two Cu-Cl distances in these compounds are comparable to those found in the related [Cu<sub>2</sub>N<sub>6</sub>Cl<sub>2</sub>] moiety in which the Cu(II) ion adopts a similar geometry.<sup>46</sup> It is worth noting that all the bridging Cu-Cl-Cu angles are smaller than 90°, between 85.03 and 87.30°. Consequently, the Cu---Cu distances are remarkably shorter (3.449-3.541 Å) than the previously reported dichloro bridged Cu(II) complexes.47,48

ELECTROCHEMICAL STUDIES. Cyclic voltammograms were recorded for 1, 2, 3 and 4 at 25 °C vs. the Ag/AgCl electrode in MeCN under a pure N<sub>2</sub> atmosphere with 0.1 M tetrabutylammonium perchlorate as the supporting electrolyte. For the three compounds, the cyclic voltammograms show three metal centered quasi-reversible waves (Fig. 3). As the dinuclear complexes convert into mononuclear  $[Cu(L^X)Cl]^+$  species in solution by the cleavage of the Cu–Cl bond (*vide infra*), the sequence of redox processes can be represented as

$$Cu^{0} \xrightarrow[]{A_{1}}{C_{1}} Cu^{I} \xrightarrow[]{A_{2}}{C_{2}} Cu^{II} \xrightarrow[]{A_{3}}{C_{3}} Cu^{III}$$
(2)

Details of peak potentials and  $E_{1/2}$  values are shown in Table 3. The  $(E_{1/2})^3$  for Cu<sup>II</sup>  $\rightarrow$  Cu<sup>III</sup> conversion is well within the range of the reported values.<sup>49</sup>

MAGNETIC PROPERTIES. The magnetic properties of the  $[Cu_2(\mu-Cl)_2(L^X)_2](ClO_4)_2$  complexes have been studied by dc susceptibility measurements on polycrystalline samples at 1000 Oe between 1.8 and 300 K. The experimental data for the four compounds are shown in Fig. 4 as a  $\chi T vs. T$  plot. As shown in Fig. 4, the  $\chi T$  product at room temperature for 1, 2, 3 and 4 ranges between 0.8 and 0.9 cm<sup>3</sup> K mol<sup>-1</sup> in good



**Fig. 3** Cyclic voltammograms of **1**, **3** and **4** (1 mmol L<sup>-1</sup>) in MeCN under a pure N<sub>2</sub> atmosphere with a sweep rate of 50 mV s<sup>-1</sup> at 25 °C with 0.1 M tetrabutylammonium perchlorate as the supporting electrolyte. The CV for **2** is supplied as ESI (Fig. S1<sup>+</sup>).

agreement with the presence of two Cu(II) S = 1/2 spin carriers considering *g* values around 2.0 and 2.2. When the temperature is lowered, the  $\chi T$  products at 1000 Oe remain roughly constant up to 25 K and then increase to reach a value at 1.8 K of 0.93 cm<sup>3</sup> K mol<sup>-1</sup> for 1, 0.97 cm<sup>3</sup> K mol<sup>-1</sup> for 2, 0.95 cm<sup>3</sup> K mol<sup>-1</sup> for 3 and 0.86 cm<sup>3</sup> K mol<sup>-1</sup> for 4. This thermal behavior clearly indicates the presence of intra-molecular ferromagnetic interactions between S = 1/2 Cu<sup>II</sup> spins.

Based on the dinuclear copper( $\pi$ ) core topology, this system can be viewed as an S = 1/2 spin dimer with the following Heisenberg spin Hamiltonian:

$$H = -2J(S_{\rm Cu1} \cdot S_{\rm Cu2}) \tag{3}$$

where *J* is the Cu<sup>II</sup>...Cu<sup>II</sup> magnetic interaction and *S*<sub>i</sub> is the spin operator for the two Cu<sup>II</sup> metal ions. The theoretical expression of the magnetic susceptibility can be estimated by applying the van Vleck equation<sup>50,51</sup> in the weak field approximation:

$$\chi_0 T = \frac{g^2 N \mu_{\rm B}^2}{k_{\rm B}} \left( \frac{2}{3 + {\rm e}^{-2J/k_{\rm B}T}} \right) \tag{4}$$

Complexes	$E_{\rm pa1}$	$E_{\rm pc1}$	$(E_{1/2})^1$	$E_{\rm pa2}$	$E_{\rm pc2}$	$(E_{1/2})^2$	$E_{\mathrm{pa3}}$	$E_{\rm pc3}$	$(E_{1/2})^3$
1	-0.229	-0.570	-0.399	0.006	-0.220	-0.107	0.570	0.280	0.425
2	-0.188	-0.587	-0.3876	0.006	-0.288	-0.282	0.630	0.260	0.445
3	-0.263	-0.544	-0.4035	0.018	-0.300	-0.141	0.616	0.180	0.398
4	-0.224	-0.545	-0.3845	0.033	-0.270	-0.119	0.546	0.324	0.435

Table 3 Cyclic voltammogram data for 1, 2, 3 and 4



Fig. 4 Magneto-structural correlation, J vs.  $\Phi/R$  plot, in  $[Cu_2(\mu-Cl)_2]^{2+}$  dinuclear complexes.

As shown in Fig. 4, very good fits of the experimental data have been achieved with  $J/k_{\rm B}$  = +0.37(2) K and g = 2.17(5) for 1,  $J/k_{\rm B}$  = +0.44(2) K and g = 2.16(5) for 2,  $J/k_{\rm B}$  = +0.47(6) K and g = 2.12(5) for 3 and  $J/k_{\rm B}$  = +0.27(6) K and g = 2.05(5) for 4. The sign of J is consistent with ferromagnetic coupling and implies that these complexes possess an  $S_{\rm T}$  = 1 triplet ground state.

MAGNETO-STRUCTURAL CORRELATION. For penta-coordinated Cu(II) involved in Cu<sup>II</sup>( $\mu$ -Cl)Cu<sup>II</sup> dinuclear complexes, the average bridging Cu–Cl–Cu angle ( $\Phi$ ) and the axial Cu····Cl<sub>axial</sub> bond distance (R) are the most important geometrical parameters that govern the sign and amplitude of the exchange-coupling constant (J). According to the empirical magneto-structural correlation established by Hatfield and co-workers,<sup>52</sup> J depends on  $\Phi/R$ . In Fig. 5, J is plotted as a function of  $\Phi/R$  and a parabolic function has been used to fit the experimental data according to ref. 48. The data extracted from the literature<sup>48</sup> are plotted in red while the present data are given in blue. We have also plotted J values obtained from DFT calculations, [single point (brown) and fully optimized (green)]  $vs. \Phi/R$  (Fig. 5), and found to be well within the range.

EPR STUDIES. The X-band EPR spectra of the copper(II) complex  $[Cu(L^{H})(Cl)]_2(ClO_4)_2$  (1), as a representative one, were performed in solid state as well as in MeOH solution at 77 K. The EPR spectrum of 1 in frozen methanol is displayed in Fig. 6. This is typical of a monomeric tetragonal Cu(II) complex with a  $d_{x^2-y^2}$  ground-state doublet. This experiment suggests that the bis(µ-Cl)-bridged species,  $[(L^X)Cu(µ-Cl)_2Cu(L^X)]^{2+}$ , undergo dissociation in solution presumably through the longer Cu–Cl (bridging) bonds (~2.88 Å), which is facilitated by additional coordination of solvent molecules.<sup>53</sup> Thus, the copper dimer complexes 1–4 are readily dissociable in solution. It is known that weakly exchange-coupled copper(II) dimers<sup>54</sup> display two signals and this is also true for the present systems.



**Fig. 5** Temperature dependence of the  $\chi T$  product for **1**, **2**, **3** and **4** at 1000 Oe (with  $\chi$  defined as molar magnetic susceptibility and equal to *M/H* per dinuclear complex). The solid lines are the best fit of the experimental data using the model described in the text.



Fig. 6 X-band EPR spectra of 1 at 77 K: (1, green) in solid state; (2, blue) in MeOH. Inset: EPR signal in the magnetic field range 100–200 mT in solid state.

The EPR spectrum in the solid state at 77 K exhibits two signals, one with  $g_{||} = 2.18$ ,  $g_{\perp} = 1.89$  and the other is a weak signal at g = 4.14 with  $\Delta M \sim \pm 1.96^{55}$  thus indicating that these complexes are dimers in solid state while in solution they are monomers. In solution at 77 K the observation that  $(g_{||} = 2.28 > g \perp = 2.025)$  with  $A_{||}(Cu) = 170$  G is consistent with a tetragonally elongated square-pyramidal geometry around the Cu(n) center and comparable to the observed spectrum for the type 2 center in the native *p*MMO ( $g_{||} = 2.24$ ,  $g_{\perp} = 2.04$  and  $A_{||}(Cu) = 185$  G).<sup>36</sup>

DFT optimized structures and molecular orbitals. Geometric parameters of  $di(\mu$ -Cl) bridged complexes (1–4) have been fully

optimized by DFT calculations in their triplet ground-state configurations. The relevant computed bond lengths and bond angles are summarized in Table 2 (in the square bracket). The computed structures in the gas phase are in relatively good agreement with the X-ray crystallographic SP-I type structures. The two Cu metal ions have a nearly planar arrangement within the N<sub>3</sub>Cl chromophore. The calculated Cu1-Cu1\_a distances are in the 3.70-3.75 Å range and are larger than the observed crystallographic data. The largest discrepancy of 0.345 Å is noted in complex 2 (L<sup>OMe</sup>) for which the crystallographic Cu1-Cu1 a distance is remarkably short in comparison to other complexes. The DFT optimized equatorial Cu1-Cl1 bond lengths for all four complexes are around 2.315 Å and the discrepancies with the X-ray data are about 0.075-0.085 Å. The agreement for the axial Cu1-Cl1\_a bond distances is even better. It is worth mentioning that only for complex 1 (L<sup>H</sup>), the calculated axial Cu1-Cl1\_a bond is shorter than the experimental one. In all the complexes, the Cu-N bond for the tertiary amino nitrogen in the equatorial plane is longer than the other two Cu-N(pyrazole) bonds. This trend is in accordance with the X-ray crystallographic data. However, the DFT optimized Cu-N bond distances are found to be always larger by 0.04-0.10 Å. In contrast to the X-ray structure with Cu1-Cl-Cu1\_a angles always below 90°, these bridging angles for the triplet ground state of the four DFT optimized complexes are always above 90°. The computed N-Cu-N and Cl-Cu-N bond angles agree well with the crystallographic data and the discrepancies are less than 6-7°. Geometries of all four complexes in their lowest singlet excited states have also been optimized to ensure that the ground state belongs to the triplet spin multiplicity. The singlet-triplet energy separations at their optimized geometries lie in the 1.36-1.45 eV range.

As seen in Table 4, there is excellent agreement between the estimated magnetic interactions from magnetic measurements and the single point DFT calculated coupling constants from the X-ray crystal structure determination. The largest discrepancy is noted for complex 4 (L<sup>Cl</sup>). The small ferromagnetic coupling constants  $(J/k_{\rm B} < 1 \text{ K})$  are the result of small energy separation between the triplet ground state and excited singlet state. However, the coupling constants become negative (i.e. antiferromagnetic with  $J/k_{\rm B} \sim -5.7$  to -7.6 K) when calculations are carried out at the triplet ground-state geometry optimized at the UB3LYP/LANL2DZ level, which is explained by the fact that Cu1-Cl-Cu1\_a bond angles increase from a ferromagnetic angle of <90° to an antiferromagnetic angle of >90° in the gas phase. Therefore, the relaxation of the geometry in the gas phase favors antiferromagnetic coupling and thus a singlet ground state. However, the small J values indicate that the two states are energetically very close. Fig. S3<sup>+</sup> shows two degenerated SOMOs (singly occupied molecular orbitals) for four complexes obtained from the DFT optimized ground state geometries. Both SOMOs are not localized on the Cu(II) centers but are delocalized mostly on (i) the  $\pi$ -orbitals of the phenyl ring and (ii) the p-orbitals of the N-atom of one of the two pyrazole rings. This delocalization from the Cu(II) centers thus

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**Table 4** Experimental and DFT calculated values of J/K and their relations with  $\Phi/R$ 

					J/K (Calc.)	
х	$\Phi/^{\circ}$ (Exp.)	<i>R</i> /Å (axial.Cu…Cl)	$\Phi/R$ (Exp.)	<i>J</i> /К (Ехр.)	X-Ray	DFT
Н	86.15	2.897	29.74	+0.37	+0.70	-5.70
OMe	85.03	2.844	29.90	+0.44	+0.90	-7.60
Ме	87.11	2.793	31.19	+0.47	+1.00	-6.00
Cl	87.30	2.830	30.85	+0.27	+1.30	-5.80



Scheme 2 Products formed in the aerial oxidation of 4-TBC.



Fig. 7 ESI-MS<sup>+</sup> (m/z) of the reaction products

increases the extent of antiferromagnetic coupling between the two Cu(II) centers.

OXIDIZING PROPERTIES. IN MeOH 4-*tert*-butyl-catechol (4-TBCH<sub>2</sub>) undergoes oxidation catalyzed by complexes 1–3 in MeOH saturated with O<sub>2</sub> [[O<sub>2</sub>] ~ 0.8 mM]<sup>56</sup> under normal atmospheric conditions. For the characterization of the oxidizing properties of the dinuclear copper(II) complexes, 4-*tert*-butyl-catechol (4-TBCH<sub>2</sub>) was used as the substrate due to its comparatively higher redox potential value ( $E_{tcc} = +0.312$  V,  $E_{4-TBC} = +0.03$  V,  $E_{catechol} = -0.046$  V,  $E_{dtbc} = -0.222$  V; all *vs.* Ag/AgCl).<sup>57</sup> The reactions in excess of 4-TBC with [Cu<sub>2</sub>(µ-Cl)<sub>2</sub>(L<sup>X</sup>)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub> in MeOH lead to the formation of 4-TBQ, 5-MeO-4-TBQ along with other minor products (Scheme 2 and Fig. 7).

Fig. 8 shows the typical time-resolved UV-Visible spectra obtained during the reaction of complex 1 with 4-TBCH<sub>2</sub> that clearly indicates the formation of 5-MeO-4-TBQ and 4-TBQ as

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Fig. 8 Time resolved absorption spectra in the visible region for the oxidation of 4-TBCH<sub>2</sub> by molecular oxygen with 1 in MeOH. The spectra were generated at a time interval of 100 seconds. Conditions are [1] = 0.5 mM, [4-TBC] = 5.0 mM, Temp. = 25 °C.

the major products. Reactions with 2 and 3 gave similar results. However, it is interesting to note that when similar reactions were carried out with complex 4 (X = Cl), no reproducible kinetic traces were found, probably due to the very fast reaction. In order to analyse the oxidation product formed during the reaction of copper(II) complexes with 4-TBCH<sub>2</sub>, the following procedure was employed. 1.0 mM complex was reacted with 1.0 mM 4-TBCH<sub>2</sub> in MeOH under aerobic conditions for 2 hours. The resulting solution was evaporated to dryness under vacuum and the solid residue was then redissolved in a minimum volume of MeCN and finally chromatographed on silica gel with MeCN as the eluent. Yellow-orange and green bands corresponding to organic products and the Cu(II) complex were collected separately and characterized spectroscopically and by mass spectrometry. It is interesting to note that the mononuclear species like  $[Cu(L^X)Cl]^+$  (X = H; FAB-mass) (422),  $[Cu(L^{X})Cl(H_{2}O)]^{+}$  (ESI-MS<sup>+</sup> (m/z) 440) and  $[Cu(L^X)Cl(MeOH)]^+$  [ESI-MS<sup>+</sup> (*m*/*z*) 453] were detected in solution after the oxidation of 4-TBCH<sub>2</sub>. The different organic oxidation products of 4-TBC are characterized by ESI-MS<sup>+</sup> (m/z) as depicted in Fig. 7. The preparative thin layer chromatography (TLC) on the mass obtained in the yellow band after vacuum evaporation using 1:10 v/v EtOAc-pet-ether (60-80 °C) as the eluent led to isolation of 1 and 2 as major products (40: 50) and minor amounts of 3, 4, 5 and 6. The existence of 3 to 6 was confirmed only by ESI-MS<sup>+</sup> analysis. Compounds 1 and 2 were further characterized by <sup>1</sup>H NMR studies.

Kinetic experiments were performed under pseudo-firstorder conditions, with the complex as a minor component and the observed rate constants ( $k_i$ ) (Table S1<sup>†</sup>) were obtained from a linear fit (initial-rate method) of the kinetic traces. All the plots of  $k_i$  vs. [4-TBCH<sub>2</sub>] yield non-linear curves of decreasing slope (Fig. 9) indicating a first-order dependence of  $k_i$  on [4-TBCH<sub>2</sub>] at lower concentration while at higher concentration the rate becomes almost independent of [4-TBCH<sub>2</sub>]. This type of rate dependence is best described by the Michaelis–Menten equation:

$$\nu = \nu_{\max}[\mathbf{S}]/(K_{\mathbf{M}} + [\mathbf{S}]) \tag{5}$$



**Fig. 9**  $k_1$  (in M s<sup>-1</sup>) vs. [4-TBCH<sub>2</sub>] plots for the oxidation of 4-TBCH<sub>2</sub>. Conditions are [**1**] = 0.5 mM; T = 25 °C. Inset shows the Lineweaver–Burk plot of  $1/\nu$  vs. 1/ [S].

Table 5 Data for catecholase activities of complexes 1-3, [c] = 0.5 mM

Complexes	$K_{\text{cat}}\left(\mathbf{h}^{-1}\right)$	$\nu_{\rm max} \left({\rm Ms}^{-1} ight)  imes 10^4$	$K_{\rm M}$ (mM)
1	648	$8.94 \pm 0.20$	$14.02 \pm 0.60$
2	50.4	$0.70 \pm 0.001$	$5.08 \pm 0.20$
3	111	$1.41 \pm 0.02$	$7.98 \pm 0.44$

 $\nu$  being the velocity of the reaction,  $\nu_{\text{max}}$  the maximum velocity that is attained when [CS], the adduct formed between S (substrate, 4-TBCH<sub>2</sub>) and C (complex), is maximum in the presence of a large excess substrate. Here, the Michaelis–Menten constant is given as  $K_{\text{M}} = (k_2 + k_{-1})/k_1$  and the corresponding reaction sequence is

$$C + S \xrightarrow{k_1} CS \xrightarrow{k_2} C + P \tag{6}$$

Non-linear fitting of data to the Michaelis–Menten equation leads to the evaluation of  $v_{\text{max}}$ , and  $K_{\text{M}}$  from which the  $K_{\text{cat}}$ rate constant for the dissociation of the complex–substrate intermediate (*i.e.*, the turnover number (TON),  $K_{\text{cat}} = v_{\text{max}}/[c]$ ) was calculated. All these parameters are listed in Table 5. We have also carried out the Lineweaver–Burk plot of  $1/\nu vs. 1/[S]$ (inset Fig. 9) and linear dependence indicates the validity of the Michaelis–Menten equation in this catalytic process.

In the oxidation of 4-TBCH<sub>2</sub> there are parallel reactions with contribution of 40:50 leading to the formation of quinone and methoxylated quinone. So it can be concluded that the Michaelis–Menten parameters ( $K_{\rm M}$ ,  $K_{\rm cat}$ ) are the sum of both the reactions.

We tried to correlate  $K_{\rm M}$  and  $K_{\rm cat}$  with Hammett  $\sigma$  parameters and plots of log ( $K_{\rm i}$ ) (i = M or cat) against  $\sigma$  give straight lines with  $\rho$  values of 1.61 ± 0.14 and 4.18 ± 0.44 for  $K_{\rm M}$  and  $K_{\rm cat}$ , respectively (Fig. 10). When we consider the  $E_{1/2}$  (Cu<sup>2+</sup>  $\rightarrow$  Cu<sup>+</sup>) of the complexes we see the following order 1<sup>H</sup> > 3<sup>Me</sup> > 2<sup>OMe</sup> which also corroborates the reactivity trend and is best explained by considering the substituent constants, although

no linear correlation for the  $E_{1/2}$  vs.  $\sigma$  plot was observed. The  $E_{1/2}$  (Cu<sup>2+</sup>  $\rightarrow$  Cu<sup>+</sup>) for 4<sup>Cl</sup> does not correspond to this trend and in solution some modified species may be formed which behaves differently. In order to check the dependence of the reaction rate on the complex concentration, experiments were carried out in the range 0.1 to 1.0 mM keeping [4-TBCH<sub>2</sub>] fixed at 1.0 mM (Table S2<sup>†</sup>). The plot of  $k_i$  vs. [complex] (Fig. S4<sup>†</sup>) is perfectly linear indicating a first-order dependence of the rate on the complex concentration.

A significantly high TON indicates that the oxidation of  $4\text{-TBCH}_2$  by molecular oxygen occurs catalytically. The reduction of molecular oxygen in the catalytic cycle may take





Scheme 3 Oxidation of the catechol to 1,2-benzoquinone

In order to test whether the catalytic oxidation of 4-TBCH<sub>2</sub> occurs through the generation of  $H_2O_2$ , at least at the initial stage of the reaction, an iodometric assay method<sup>60</sup> based on the spectrophotometric determination of  $[I_3^-]$  was adopted. In the presence of  $H_2O_2$ , a characteristic absorption band is observed at 353 nm ( $\varepsilon = 26\,000 \text{ M}^{-1} \text{ cm}^{-1}$  in water). The corresponding amplitude of the absorption band is almost the same as that found in the blank experiments carried out in the absence of catechol but in the presence of 4-TBQ and the active complex. So, it can be concluded that in the catalytic cycle molecular oxygen undergoes  $4e^-$  reduction to  $H_2O$  instead of  $2e^-$  reduction to  $H_2O_2$ .

The following observations are pertinent for framing the mechanism of the oxidation of  $4\text{-TBCH}_2$  as outlined in Scheme 4.

(i) Complexes in solution (MeOH) undergo rapid decomposition to the corresponding mononuclear entities  $[Cu(L^X)Cl]^+$ and support comes from the following observations: (a) The EPR spectrum in MeOH at 77 K is typical for mononuclear copper( $\pi$ ) complexes. (b) FAB-mass spectra of the reaction immediately after the initiation of the reaction show a prominent peak for  $[Cu(L^H)Cl]^+$  or  $[Cu(L^H)Cl]_2^{2+}$  (422) while ESI-MS<sup>+</sup> (*m*/*z*) mass spectra reveal the presence of  $[Cu(L^H)Cl(H_2O)]^+$ (440) and  $[Cu(L^H)Cl-(MeOH)]^+$  (453). The two copper( $\pi$ ) centers may be equally coordinated by two solvent molecules to justify the dinuclear structure with ESI-MS<sup>+</sup> (*m*/*z*) 440 (H<sub>2</sub>O) and



Scheme 4 Oxidation of the 4-TBCH<sub>2</sub> to 5-methoxy-4-TBQ

453 (MeOH). But there is a problem because copper(II) centers in the parent complexes are already in 5-coordinated distorted square pyramidal geometry and due to the presence of two bulky 3,5-dimethylpyrazole groups around each copper(II) center it is very difficult to accommodate a solvent molecule to get octahedral geometry. So one can safely assume that the dimer splits in solution to give monomers (Scheme 5). Moreover, (c) conductivity measurements of the pure complex in MeCN give an equivalent conductance of 150 (mho) which is typical for a 1:1 electrolyte.

(ii) The dependence of initial rate  $(k_i)$  on the concentration of  $[Cu_2(L^H)_2Cl_2](ClO_4)_2$  was checked by varying the concentration in the range 0.01–0.50 mM, keeping 4-TBCH<sub>2</sub> concentration fixed at 1 mM (Table S3<sup>†</sup>). A plot of  $k_i vs.$  $[Cu^{II}_2Cl_2(L^X)_2^{2^+}]$  or  $2[CuL^XCl]^+$  gives a straight line (Fig. S4<sup>†</sup>) manifesting a first-order dependence on complex concentration precluding the possibility of existence of di  $\Rightarrow$  mono equilibrium, particularly in the experimental range of complex concentration.

(iii) Oxidation of 4-TBCH<sub>2</sub> occurs *via*  $4e^-$  reduction of O<sub>2</sub> leading to the formation of H<sub>2</sub>O.

(iv) The externally added LiCl was found to reduce the reaction rates of oxidation of 4-TBCH<sub>2</sub> [Fig. S5<sup>†</sup>] supporting the fission of the longer Cu–Cl (bridging) bond in a dimer to form monomers which is further facilitated by externally added Cl<sup>-</sup>. The inner-sphere association between a complex and 4-TBCH<sub>2</sub> is thought to be more facile in the case of  $[CuL^{X}(Cl)(MeOH)]^{+}$  than  $[CuL^{X}(Cl)_{2}]$  clearly explaining the slight inhibition of reaction rates by externally added Cl<sup>-</sup>.

(v) The splitting of a dimer to monomers is further supported by considering mono-phenoxo-monochlorodicopper (MPD) as one of the reaction intermediates generated from  $[Cu(L^{H})Cl]_{2}^{2+}$  and 4-TBCH<sub>2</sub>; but the optimized structures reveal its splitting into two isolated monomers (MPD') ( $[Cu(L^{H})-(4-TBC-2H)]$  and  $[Cu(L^{H})Cl]^{+}$ ) probably due to steric crowding around the metal centers (Fig. 11).

 $[Cu_{2}(L^{X})_{2}(Cl)_{2}]^{2+}$   $(L^{X})_{2}(Cl)_{2}]^{2+}$   $(L^{X})_{2}(Cl)_{2}]^{2+}$   $(L^{X})_{2}(Cl)_{$ 

Scheme 5 Splitting of mother complexes in solution phase.



Fig. 11 Splitting of  $[Cu_2(\mu-CI)(4-TBCH_2-H)(L^H)_2]^{2+}$  into  $[Cu (L^H)_2(\mu-CI)]^+$  and  $[Cu-(L^H)(4-TBCH_2-2H)]$  revealed from DFT calculations.



**Fig. 12** Time resolved spectra for the reaction between  $[Cu_2(L^H)_2(CI)_2]^{2+}$  and 4-*tert*-butylcatechol in MeCN. Conditions: [C] = 2.0 mM, [4-TBCH<sub>2</sub>] = 10.0 mM, T = 32 °C.

(vi) The appearance of a peak at 386 nm may be attributed to the formation of a free or bound semiquinone radical.<sup>61</sup> Inhibition of the reaction rate by the added Cl<sup>-</sup> concentration was observed which indicates that there is a dissociation of the longer Cu-Cl bridging bond to facilitate the coordination of catechol to one Cu-atom in the complex moiety. In order to get some idea that the semiguinone-bound Cu-species formed during the course of the reaction, 4-TBCH<sub>2</sub> was reacted with the complex at higher concentration ([complex] = 2 mM,  $[4\text{-TBCH}_2] = 10 \text{ mM}$  and a peak in the region 500–600 nm was gradually built up (Fig. 12), which clearly indicates the formation of a metal-bound semiquinone radical anion as previously observed.<sup>62</sup> We have also tried to check the formation of Cu<sup>I</sup>-semiguinone species by an electrochemical method but failed to detect such species; this may be due to its very fast decomposition on the electrode surface (beyond the diffusion limit) precluding its accumulation to the detection limit. But in the reaction mixture there is a definite signature of  $[Cu(L^{H})]$  $Cl(4-TBCH_2-H^+)$  in the FAB mass [(III) + K<sup>+</sup> = 626].

All the foregoing observations lead us to frame a reaction mechanism as outlined in Scheme 5. Here, the molecular dioxygen binds to the semiquinone radical at the C5 position and is transformed into a peroxyl radical, which in turn coordinates to the metal center to form a seven-membered ring and concomitantly oxidizes the metal center to Cu(II). Breakdown of the peroxo-linkage as well as Cu<sup>II</sup>-OAr may be anticipated to occur through the formation of a five-membered ring in the transition state which ultimately gives [Cu<sup>II</sup>(L<sup>H</sup>)(OH)Cl]  $[ESI-MS^{+} of Cu^{II}(L)(OH)Cl + H^{+} = 440.9], H_2O and 5-methoxy-4-$ TBQ. The [Cu<sup>II</sup>(L)(OH)Cl] then reacts with catechol to regenerate the original catalyst  $[L^{X}Cu-Cl]^{+}$  and  $H_{2}O$  to complete the catalytic cycle. When we carried out the catalytic oxidation of 3,5-di-tert-butyl catechol (3,5-di-Bu<sup>t</sup>-TBCH<sub>2</sub>) we did not get any oxygenated product, as in the case of 4-TBCH<sub>2</sub>, instead 100% 3,5-di-tert-butyl-o-quinone is formed (Fig. S5<sup>†</sup>). The failure to get the oxygenated product in the case of 3,5-di-Bu<sup>t</sup>-TBCH<sub>2</sub> may be attributed to the fact that electrophilic site C5 is already occupied and does not allow the attack by molecular

oxygen on to it. In the present case the attack of molecular oxygen on C5 and Me transfer from the solvent (MeOH or MeCN) are in line with the previous observations made by Ali *et al.*<sup>63</sup> The methyl group in MeO comes from the solvent, which is verified by carrying out the same experiments in MeCN, which also gives 5-MeO-4-TBQ in comparable yield as in the case of reactions in MeOH. Thus it manifests the fact that the oxygen molecule attacks C5 to generate the transient intermediate (**V**) which rapidly transforms to  $[Cu(L^X)(OH)(Cl)]$ .

The formation of 6,6'-Bu<sup>t</sup>-biphenyl-3,4,3',4'-tetraol as a minor product may be facilitated by the reaction of a part of 4-TBQ formed in the reaction with catechol (Scheme 6). This



**Scheme 6** Oxidation of the catechol by 4-Bu<sup>t</sup>-1,2-benzoquinone to 6,6'-Bu<sup>t</sup>-biphenyl-3,4,3',4'-tetraol.

The above mechanism is further supported by the DFT optimization of various probable intermediates and considering their energies. The dichloro species  $[Cu_2(L^X)_2(Cl)_2]^{2+}$  splits into two monopositive monomers which get coordinated with water and/or methanol. Each of the three monomers was fully optimized at the B3LYP/LANL2DZ level of calculations and was found to be stable as confirmed from their vibrational frequency calculations. However, DFT calculations reveal that such a splitting is energetically favorable by about -49.2 kcal  $mol^{-1}$ . It has been observed that when  $[Cu(L^X)(Cl)]^+$  is coordinated with H<sub>2</sub>O and MeOH, the stabilization energies are -13.7 and -12.9 kcal mol<sup>-1</sup>, respectively. The reaction of the solvent coordinated complex (I) with catechol (II) favors the formation of (III). The DFT calculated energy of stabilization is about -54 kcal mol<sup>-1</sup>. The calculations further establish that other possible products IIIa, IIIb and IIIc are energetically less stable. We have fully optimized the geometries of intermediates (VI) and (VII), which are found to be stable. In the presence of oxygen and methanol, the intermediate (III) transforms into (VI) and (VII) through a proposed transition structure (V). The energy lowering during this process is



Fig. 13 DFT optimized structures proposed in framing the mechanism.

calculated to be -43.9 kcal mol<sup>-1</sup>. Other intermediates  $[Cu^{III}=O(L^X)Cl]$  (VIII) (136 kcal mol<sup>-1</sup>) and  $[Cu^{III}(OH)(L^X)]^+$  (IX) (114 kcal mol<sup>-1</sup>) were precluded over (VII). It may be mentioned here that singlet oxygen is involved in this transformation as is found in the biological systems. The formation of  $[Cu(L^H)(Cl)_2]$  (X) from  $[Cu(L^H)(Cl)]^+ +Cl^-$  (externally added) has also been checked through DFT calculations and was found to be favored by ~ -116 kcal mol<sup>-1</sup> and supports the inhibition of the reaction in the presence of added Cl<sup>-</sup> (Fig. 13). The details of DFT calculations and energies are listed in Table S4.<sup>†</sup>

In summary, four bis(µ-Cl) complexes of pyrazole-based tridentate tripodal ligands have been synthesized and characterized structurally. Both the copper centers in dinuclear complexes are penta-coordinated with SP-I geometries sharing a base-apex edge with parallel basal planes. Cryomagnetic studies reveal that copper(II) centers in each complex are weakly ferromagnetically coupled with J = 0.47-0.27. All these complexes showed very good magnetostructural correlation within the framework of SP-I categories of dinuclear copper(II) complexes. All these complexes with nitrogen donor atoms from pyrazole based ligands can be considered as the active site of the copper monooxygenases enzyme and indeed complexes 1-3 displayed monooxygenase activity oxidising 4-TBCH<sub>2</sub> in methanol by molecular oxygen to give 4-tert-butyl-5-methoxy-o-quinone as one of the major products. A mechanism has been proposed in which the Cu<sup>I</sup>-semiquinone radical intermediate, formed through intramolecular electron transfer from phenol to  $Cu(\pi)$ , is attacked by the molecular dioxygen and forms a bond at the C5 position of the benzene ring leading to the oxidation product 5-MeO-4-TBQ and  $[Cu(L^{X})(Cl)(OH)]$ . The latter product then reacts with 4-TBCH<sub>2</sub> to form  $[Cu(L^X)(Cl)(4-TBCH)]$ , the initial intermediate of the catalytic cycle.

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