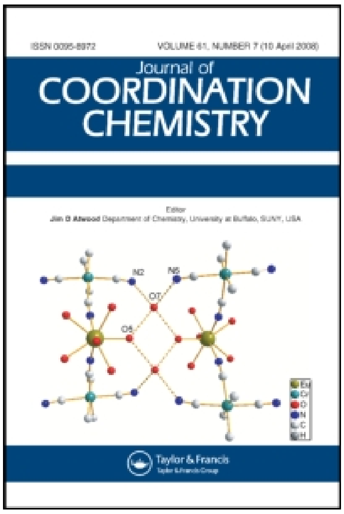

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Homogeneous oxidative coupling catalysts: stoichiometry and product characterization of the oxidation of copper(I) complexes $[(Pyr)_nCuX]_4$ ($n = 1$ or 2, Pyr = pyrrolidine, $X = Cl, Br$ or I) by dioxygen in aprotic media

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Copper(I) halides react quantitatively with pyrrolidine (Pyr) in dioxygen-free methylene chloride or nitrobenzene to form tetranuclear copper(I) complexes $[(Pyr)_nCuX]_4O_2$; $n = 1$ or 2, $X = Cl$, Br or I. These complexes are very soluble and completely reduce dioxygen to a dioxo bridging ligand with stoichiometry, $\Delta[Cu(I)]/\Delta[O_2] = 4.0$. Analytical and cryoscopic data establish the formation of discrete tetranuclear products. The stable oxo solids $[(Pyr)_nCuX]_4O_2$ mimic the tyrosinase copper protein and are homogeneous oxidative coupling catalysts for phenols. Electronic transition spectra in the near infrared for $[(Pyr)_nCuX]_4O_2$ are explained as charge transfer from a minimum of three halo ligands to a copper(II) site, (LMCT). Therefore, one can expect a higher molar absorptivity when $X = I$, as in the $[(Pip)_nCuX]_4O_2$ system. However, molar absorptivity is about half of expected. The lower absorptivity explains the step structure of $[(Pyr)_nCuI]_4O_2$, in which only two copper(II) sites, instead of four as in $[(Pyr)_nCuX]_4O_2$, $X = Cl$ or Br, have three iodo ligands per copper center. In addition to infrared and electronic spectra for $[(Pyr)_nCuI]_4O_2$, EPR bands are observed, and it is concluded that two different types of copper(II) sites are present as represented in scheme 1.

Keywords: Tetranuclear oxo copper(II); Homogeneous oxidative coupling catalysts

1. Introduction

Copper plays an important role in activation of dioxygen and in catalytic processes involving dioxygen but understanding of the products of aprotic copper(I)-dioxygen reaction is still challenging [1–3].

Although copper(II) has varied coordination chemistry [4], the corresponding chemistry of copper(I) is still being developed, in part because of the experimental difficulties connected with the dioxygen sensitivity of copper(I) complexes [2]. The copper(I)/copper(II) couple differs from other dioxygen-sensitive couples in that one of the oxidation states involved has a completely filled d-orbital.

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There are three other major impediments to advancing our knowledge of dioxygen systems which depend on a copper(I)-dioxygen interaction. The first has evolutionary origin that leaves copper centers in flexible ligand systems in plants and lower animals [5]. The second is the great tendency of low molecular weight copper(I) systems to completely reduce dioxygen under aprotic conditions [6–15]. An important driving force for complete dioxygen reduction is formation of strong oxocopper(II) bonds. Unfortunately, no detailed structure of a simple oxocopper(II) species is presently known, largely due to difficulties of crystallization in the absence of disproportionation [6–15]. Structural information may ultimately come from conversion of oxocopper(II) species to carbonato analogs by carbon dioxide [16, 17]. The third impediment is the tendency of the products of aprotic oxidation of low molecular weight copper(I) complexes to catalyze oxidation of their own ligands [18], leading to model systems which are constantly changing in the presence of excess dioxygen.

The objective of this work is generalization of the discovery of $[(\mathrm{Pip})_n\mathrm{CuX}]_4\mathrm{O}_2$; Pip = piperidine, X = Cl, Br or I [6] by isolation of stable solids which are catalysts for oxidative coupling of 2,6-dimethylphenol (DMP) to 3,3′,5,5′-tetramethyl-4,4′-diphenoquine (DPQ) and oxidation of iodo derivatives to form the oxo analog, which were impossible in pyridine systems [7, 9, 13].

Pyrrolidine was the chosen candidate for this study with basicity ($\mathrm{pK}_b = 2.73$) close to that of piperidine ($\mathrm{pK}_b = 2.80$) and with a free pyrrolidyl hydrogen which can form a hydrogen bond.

2. Experimental

2.1. *Materials*

Pyrrolidine, Pyr (Aldrich), was used as received. Copper(I) halides were prepared as described in the literature [19].

Nitrobenzene was distilled under reduced pressure from P_4O_{10} and stored over 4 Å molecular sieves. Methylene chloride was washed with concentrated sulfuric acid, dried over sodium carbonate, refluxed over P_4O_{10}, then distilled and stored over anhydrous sodium carbonate [9].

High purity dinitrogen was deoxygenated by passing through a column of Alfa-DE-OX solid catalyst and dried by passage through a 60 cm column of dehydrated silica gel and 30 cm column of calcium chloride and molecular sieves.

2.2. *Synthesis of* $[(Pyr)_nCuX]_4O_2$ ($n = 1$ *or* 2, $X = Cl, Br$ *or* I)

A solution of Pyr (2.5 mmol for $n = 1$ and 5 mmol for $n = 2$) was dissolved in anhydrous methylene chloride under dinitrogen at 25°C. CuX (2.5 mmol) was then added and the mixture was stirred with a stream of dinitrogen until the solid dissolved, giving a yellow solution for X = Cl, a yellowish-orange solution for X = Br and a reddish-orange solution for X = I. Then this solution of $[(\mathrm{Pyr})_n\mathrm{CuX}]_4$ was flushed with dioxygen. Immediate oxidation occurred, the solution turning to deep green for X = Cl or Br and greenish brown for X = I. After 10 min, the gas steam was stopped. After centrifuging the desired solution, the solvent was removed in a vacuum rotary evaporator, leaving a green solid of di-μ-oxotetranuclear copper(II) products; $[(Pyr)_nCuX]_4O_2$; $n = 1$ or 2, X = Cl, Br or I.

Solvent evaporation after gel permeation chromatography for redissolved solid products in methylene chloride, using flash column under dry dinitrogen gas, on Biobeads SX–12 resin with methylene chloride as an eluent, gave the same desired product $[(Pyr)_nCuX]_4O_2$.

Attempted crystallization of oxo copper(II) derivatives with different procedures failed to produce a single crystal of $[(Pyr)_nCuX]_4O_2$.

Dissolved complexes were identified by cryoscopic molecular weight determination in nitrobenzene (m.p. = 5.7°C, freezing point depression constant, $K_f = 7.0^{\circ}C/molal$) [12], using a Eutechnics precision temperature model 4600 thermometer.

The elemental copper and halogen (Cl and Br) contents were determined as in the literature [20]. All other elemental analysis were determined at the Microanalytical Laboratory, Chemistry Department, Cairo University, Egypt. Molecular weights and analytical data for the isolated complexes are collected in table 1.

2.3. *Physical measurements*

Electronic spectra for ligand and products in methylene chloride or nitrobenzene were measured with a Shimadzu 160A ultraviolet-visible recording spectrophotometer in matched quartz cells at room temperature.

FT-IR spectra of KBr disks for solid products or KBr plates for liquid ligands were obtained with a Shimadzu Model 8108 spectrophotometer at room temperature. The 906.5 or 3026.3 cm^{-1} absorptions of polystyrene were used for calibration.

EPR spectra of samples of pyrrolidine complexes were measured at the King Fahd University of Petroleum and Minerals on a Radiopan Varian spectrometer at 100.00 KHz and at different G modulation amplitudes with a rectangular TE 102 cavity and a 100 KHz modulation field. Resonance conditions were found at ca 9.7 GHz (X-band) at room temperature only. The field was calibrated with a powder of diphenylpicrylhydrazyl (DPPH; $g = 2.0037$) [21].

Cyclic voltammetry measurements were carried out using a bioanalytical system BAS-27 electrochemistry analyzer connected to a BAS X-Y recorder and in conjunction with a three-electrode cell fitted with a purged dinitrogen gas inlet and outlet. The three electrodes were a Beckman platinum working electrode (flat circular sheet of

Table 1. Analytical and cyroscopic data for $[(Pyr)_nCuX]_4O_2$, $n = 1$ or 2, X = Cl, Br or I, Pyr = pyrrolidine.

	Anal.[a] (%)					
Complex	C	H	N	X	Cu	Molecular weight[b]
$[(Pyr)CuCl]_4O_2$	27.2 (27.0)	5.0 (5.0)	7.8 (7.8)	19.7 (19.9)	35.0 (35.4)	729 ± 20 (713)
$[(Pyr)CuBr]_4O_2$	21.4 (21.5)	4.0 (4.0)	6.2 (6.2)	35.6 (35.7)	28.7 (28.4)	890 ± 20 (895)
$[(Pyr)CuI]_4O_2$	21.4 (18.4)	3.7 (3.4)	6.0 (5.4)	–	23.0 (23.5)	1088 ± 20 (1078)
$[(Pyr)_2CuCl]_4O_2$	35.6 (36.5)	7.1 (7.2)	11.2 (11.2)	14.4 (14.2)	25.3 (25.4)	1003 ± 20(997)
$[(Pyr)_2CuBr]_4O_2$	32.7 (32.5)	5.6 (6.1)	9.6 (9.4)	27.7 (27.1)	20.9 (21.5)	979 ± 20 (1179)
$[(Pyr)_2CuI]_4O_2$	26.9 (28.1)	5.0 (5.2)	8.2 (8.2)	–	19.3 (18.5)	1135 ± 20 (1363)

[a] Calculated values in parentheses.

[b] Measured in nitrobenzene at (3–5) × 10^{-2} molal level [12].

5 mm diameter) and a platinum wire auxiliary electrode. All potentials were measured with respect to Ag/Ag^+ (1.0×10^{-3} M $AgNO_3$ in 0.1 M tetrabutylammonium perchlorate (TBAP) in methylene chloride) as the non-aqueous reference electrode [22, 23]. The measurements were performed at room temperature in methylene chloride containing 0.1 M TBAP, 1.0×10^{-3} M copper complexes deoxygenated by bubbling them with dioxygen free dinitrogen gas.

2.4. *Dioxygen uptake measurements*

The stoichiometry of the oxidation of copper(I) complexes by molecular dioxygen in methylene chloride and in nitrobenzene was established over a wide range of concentration (0.2–8×10^{-4} M) for each copper(I) complex. A representative reaction was carried out as follows: CuX (X = Cl, Br or I) was weighed into a 100 mL three-neck round bottom flask filled with a gas inlet tube (connected to the Warburg apparatus [24], which was fitted with dioxygen gas at room temperature and atmospheric pressure), pressure equalizing dropping funnel, and magnetic stirrer. The pyrrolidine ligand (Pyr) in methylene chloride or nitrobenzene (saturated with dinitrogen gas in the dropping funnel) was added with stirring to CuX (X = Cl, Br or I) and the reaction was allowed to take place until no more dioxygen was consumed. The initial and final volumes were calculated at room temperature and atmospheric pressure.

2.5. *Test of catalytic activity*

Solutions of various copper(II) complexes $[(Pyr)_nCuX]_4O_2$ in methylene chloride were added to separate samples of a 100-fold excess of 2,6-dimethylphenol (DMP) in methylene chloride. Dioxygen was then bubbled through each solution for 15 min. 3,3′,5,5′-tetramethyl-4,4′-diphenoquinone (DPQ) was identified by comparison with an authentic sample (for DPQ molar absorptivity $= 5.05 \pm 0.01 \times 10^4\,M^{-1}\,cm^{-1}$ at 431 nm).

3. Results and discussion

Copper(I) halides react quantitatively with pyrrolidine (Pyr), ($pK_b = 2.73$) in dioxygen-free weakly coordinating aprotic solvents such as methylene chloride or nitrobenzene to form tetranuclear complexes $[(Pyr)CuX]_4$ for $n = 1$, in which Cu(I) exists in a four-coordinate environment, equation (1), and tetranuclear complexes $[(Pyr)_2CuX]_4$ for $n = 2$, in which each Cu(I) center is coordinated to five ligands, equation (2).

$$4Pyr + 4CuX \longrightarrow [(Pyr)CuX]_4 \tag{1}$$

$$8Pyr + 4CuX \longrightarrow [(Pyr)_2CuX]_4 \tag{2}$$

Attempted isolation of the copper(I) complexes $[(Pyr)_nCuX]_4$ gave extremely air-sensitive solids that failed to give reproducible analytical data. However, cryoscopic measurements on the solution in nitrobenzene at 5°C indicated formation of tetrameric $[(Pyr)_nCuX]_4$.

3.1. *Structures of* $[(Pyr)_nCuX]_4$

Although molecular structure of copper(I) complexes $[(\mathrm{Pyr})_n\mathrm{CuX}]_4$ are not determined, the close similarity between pyrrolidine (pyr) and piperidine (Pip) ligands (both having free N–H and close values of $\mathrm{pK}_b = 2.75 \pm 0.05$) [6] suggest molecular core structure for $[(\mathrm{Pyr})_n\mathrm{CuX}]_4$ similar to that reported for $[\mathrm{LCuI}]_4$, L = pyridine, N,N-diethylnicotinamide (DENC) or piperidine [9, 25, 26]. Tetrameric molecules are built up by an inner tetrahedral Cu_4 cluster surrounded by a concentric and opposed larger I_4 tetrahedron with each I attached to three coppers.

3.2. *Reactivity of* $[(Pyr)_nCuX]_4$; n = 1 *or* 2 *and X = Cl, Br or I with dioxygen*

Dioxygen uptake measurements were consistent with a reaction stoichiometry given by equation (3).

$$[(\mathrm{Pyr})_n\mathrm{CuX}]_4 + \mathrm{O}_2 \longrightarrow [(\mathrm{Pyr})_n\mathrm{CuX}]_4\mathrm{O}_2 \qquad (3)$$

The stoichiometry, $\Delta[\mathrm{Cu(I)}]/\Delta[\mathrm{O}_2] = 4.0$, is expected in systems involving non-oxidizable ligands. Cryoscopic and analytical data for the reaction products are listed in table 1. The cryoscopic data indicate that $[(\mathrm{Pyr})_n\mathrm{CuX}]_4\mathrm{O}_2$ complexes, like their copper(I) precursors, are discrete tetranuclear species with no tendency to disproportionate (unlike oxidation products $[\mathrm{L}_n\mathrm{CuX}]_4$, L = pyridine) [12, 27, 28] or polymerize as found in oxocopper(II) species with alkyldiamine ligands [12, 15].

Although these oxidation products are quite stable in solutions or as solids in the absence of moisture, attempts to crystallize $[(\mathrm{Pyr})_n\mathrm{CuX}]_4\mathrm{O}_2$ complexes from methylene chloride/ether are frustrated by a tendency towards disproportionation on diffusion of dry ether as precipitating solvent into their methylene chloride solutions. One of the disproportionation products is $(\mu_4\text{-O})(\mathrm{Pyr})_4\mathrm{Cu}_4\mathrm{Cl}_6$. Such a $(\mu_4\text{-O})$ is similar to the well-known structure of $(\mu_4\text{-O})\mathrm{Py}_4\mathrm{Cu}_4\mathrm{X}_6$ [29a] and $(\mu_4\text{-O})\mathrm{L}_4\mathrm{Cu}_4\mathrm{Cl}_6$ (L = N, N-dimethylaminomethyl ferrocene) [29b].

3.3. *Infrared spectra*

The major features of the IR spectra of free pyrrolidine and $[(\mathrm{Pyr})_n\mathrm{CuX}]_4\mathrm{O}_2$, $n = 1$ or 2, X = Cl, Br or I, as KBr discs are provided as Supplementary Material. Free pyrrolidine shows a very strong symmetrical broad band centered at 3421 cm^{-1} due to ν_{NH} and two sharp strong bands of about equal intensity centered at 1653 and 1520 cm^{-1} due to δ_{NH}. The relative intensity of ν_{NH} is higher than the bands corresponding to δ_{NH}. On complexation, the following changes in ν_{NH} and δ_{NH} for pyrrolidine ligands in $[(\mathrm{Pyr})_n\mathrm{CuX}]_4\mathrm{O}_2$, $n = 1$ or 2 and X = Cl, Br or I, are observed: (a) For $[(\mathrm{Pyr})\mathrm{CuX}]_4\mathrm{O}_2$, X = Cl or Br, the strong symmetrical broad band for ν_{NH} is split into two bands of different intensity, one centered at 3447 cm^{-1} and a more intense band at 3337 cm^{-1} for X = Cl. The two strong bands for δ_{NH} overlapped to one centered at 1622 cm^{-1} with two shoulders at lower wavenumbers for X = Cl. The relative intensity of ν_{NH} was higher than the intensity of δ_{NH}. (b) On changing X from Cl or Br to I, the strong ν_{NH} of the ligand is centered at 3435 cm^{-1} with a very weak shoulder at 3280 cm^{-1}. For δ_{NH} the two bands overlapped and centered at 1631 cm^{-1} with two shoulders at lower wavenumbers as for X = Cl or Br in addition to a shoulder at higher wavenumber.

Table 2. Room temperature solid-state X-band EPR spectra and electronic spectral data for $[(Pyr)_nCuX]_4O_2$, $n = 1$ or 2, X = Cl, Br or I, in methylene chloride.

	EPR							
Complex	$A_{\parallel}^{a}$	$g_{\parallel}$	$g_{\perp}$	g_1	g_2	g_3	$\langle g \rangle^{b}$	λ_{max} (nm) ($\in_{\lambda max}$ ($M^{-1}\,cm^{-1}$))
$[(Pyr)CuCl]_4O_2$				2.27	2.09	2.03	2.13	740 (458); 830 (450)
$[(Pyr)CuBr]_4O_2$	–	–	–					760 (788);830 (788)
$[(Pyr)CuI]_4O_2$	95.2	2.18	1.98				2.05	710 (479)
$[(Pyr)_2CuCl]_4O_2$	268.7	2.00	2.19				2.13	740 (554); 830 (536)
$[(Pyr)_2CuBr]_4O_2$	178.5	2.20	1.98				2.05	740 (673);830 (615)
$[(Pyr)_2CuI]_4O_2$	214.2	2.33	1.98				2.10	700 (190)

[a] Units are $10^{-4}\,cm^{-1}$.

[b] $\langle g \rangle = 1/3\ (g_{\parallel} + 2g_{\perp})$ or $\langle g \rangle = 1/3\ (g_1 + g_2 + g_3)$.

The relative intensity of δ_{NH} is stronger than ν_{NH}, which was not the case when X = Cl or Br as for the free pyrrolidine. (c) For $[(Pyr)_2CuX]_4O_2$, X = Cl, Br or I, the band corresponding to ν_{NH} for free pyrrolidine split into two bands as for $[(Pyr)CuX]_4O_2$, X = Cl or Br, but the more intense one was at higher wavenumber. For δ_{NH}, as for one pyrrolidine per each copper, the two strong bands overlap to one intense band with two shoulders for X = Cl and Br and four shoulders for X = I. When the number of pyrrolidine ligands around each copper increased from one to two, the relative intensity of δ_{NH} becomes stronger than ν_{NH}, which was not the case for free pyrrolidine or for pyrrolidine in $[(Pyr)CuX]_4O_2$, X = Cl, Br or I.

One can conclude that the hydrogen of the free NH in pyrrolidine is very sensitive to the core structure and how that hydrogen interacts with the core. The interaction of pyrrolidine in $[(Pyr)CuX]_4O_2$ was similar for X = Cl or Br and different for X = I. For $[(Pyr)_2CuX]_4O_2$, the pyrrolidinyl hydrogen for each pyrrolidine interacts differently.

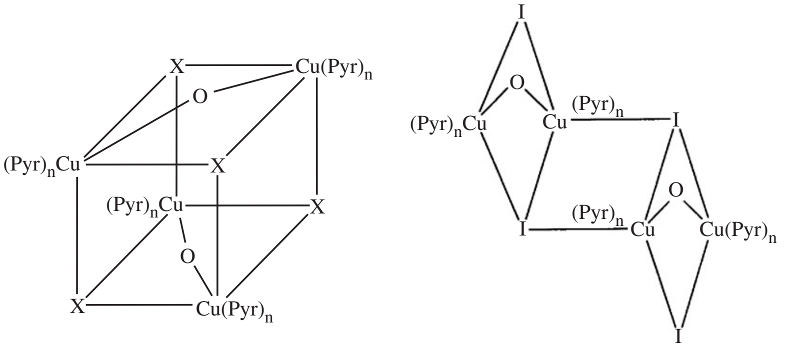
3.4. *Electronic spectra*

Electronic spectral data for $[(Pyr)_nCuX]_4O_2$, $n = 1$ or 2, X = Cl, Br or I, are listed in table 2 and illustrated in Supplemental Material. For X = Cl or Br in $[(Pyr)_nCuX]_4O_2$, $n = 1$ or 2, split maxima in the range 740–840 nm are observed for all the complexes regardless of $n = 1$ or 2. Molar absorptivities ($\in$, $M^{-1}\,cm^{-1}$) of the split maxima are very sensitive to the type of halo ligand ($\in$ for Br > Cl), as shown in table 2 and Supplemental Material.

Similar to $[(Pip)_nCuX]_4O_2$, $n = 1$ or 2, X = Cl, Br or I [26], as the electronegativity of X decreased (i.e.., the radius of X increased) molar absorptivities increased. Therefore, one can conclude a charge transfer transition from a minimum of three halo ligands to a copper(II) site (LMCT).

When X = I in $[(Pyr)_nCuX]_4O_2$, the system behaves differently from X = Cl or Br, as seen in the piperidine system [6]. The broad band is split at 870 nm and 710 nm with low absorptivity when compared to the Cl or Br analog, shown in table 2 and Supplemental Material.

When X = I, the infrared of NH in pyrrolidine (ν_{NH} and δ_{NH}) behave differently than for X = Cl or Br.



$[(Pyr)_nCuX]_4O_2$, X = Cl or Br

$[(Pyr)_nCuI]_4O_2$

Scheme 1. Proposed molecular core structure for $[(Pyr)_nCuX]_4O_2$, $n = 1$ or 2, X = Cl, Br or I.

Such differences for X = I lead us to conclude that the structure of $[(Pyr)_nCuI]_4O_2$ is not a cubane like $[(Pyr)_nCuX]_4O_2$, X = Cl or Br, but more likely to be a step structure, scheme 1. For a step structure of $[(Pyr)_nCuI]_4O_2$, $n = 1$ or 2, there are only two copper(II) sites instead of four as in X = Cl or Br that have three iodo ligands per copper.

3.5. *EPR spectra*

Room temperature solid-state EPR spectra of $[(Pyr)_nCuX]_4O_2$, $n = 1$ or 2, X = Cl, Br or I, are summarized in table 2 and shown in Supplemental Material.

For $n = 1$ and X = Cl, a rhombic spectrum with lowest $g < 2.03$ is observed. Such a spectrum is characteristic of a copper(II) center in compressed rhombic symmetry with distorted trigonal bipyramidal geometry [30]. For $n = 1$ and X = I, the EPR spectrum shows an axial spectrum with lowest $g < 2.03$. The spectrum has more bands which could be due to overlap between copper(II) sites with compressed trigonal bipyramidal stereochemistry and copper(II) sites with compressed rhombic symmetry as in scheme 1.

For $n = 2$ and X = Cl, Br or I, the spectra are axial with lowest $g < 2.03$. Therefore, the spectra for X = Cl or Br are consistent with copper(II) in axial symmetry with all principal axes aligned parallel for compressed tetragonal-octahedral geometry [31]. However, for X = I more bands are observed, suggesting two different types of copper(II) sites, compressed tetragonal octahedral and compressed trigonal-bipyramidal, as represented in scheme 1.

3.6. *Redox chemistry*

Cyclic voltammetric (CV) measurements for $[(Pyr)_nCuX]_4O_2$, $n = 1$ or 2 and X = Cl or Br, were performed in methylene chloride containing 0.1 M tetrabutylammoniumperchlorate (TBAP). The data are represented in table 3 and shown in Supplementary Material. All voltammograms are irreversible. For $n = 1$ and X = Cl, the voltammograms show two cathodic peaks at −0.75 V and −1.1 V. On changing n from 1 to 2

Table 3. Cyclic voltammetric data for $[(Pyr)_nCuX]_4O_2$, $n=1$ or 2, X = Cl or Br, at a scan rate 100 mV sec^{-1} at room temperature in 0.1 M TBAP in methylene chloride.

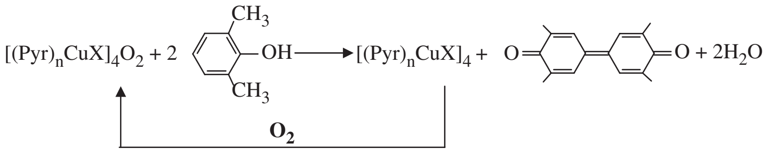
Complex	Cathodic peaks (volts)	Anodic peaks (volts)
Ferrocene[a]	−0.25	0.05
$[(Pyr)CuCl]_4O_2$	0.75, −1.1	0.62
$[(Pyr)_2CuCl]_4O_2$	−0.70	0.65
$[(Pyr)CuBr]_4O_2$	−0.82, −1.07, −1.18	0.76

[a] 0.4 Volt is the formal electrode potential of a reversible one-electron standard ferrocene/ferrocenium ion couple (Fe/Fe^+) *vs.* normal hydrogen electrode (NHE) [23, 30].

for X = Cl, reduction of copper(II) centers are averaged at one cathodic peak potential (−0.7 V). On changing X from Cl to Br for $n=1$, more reduction peaks are observed, which usually happens when Cl is changed to Br or I in similar core structures [6].

3.7. *Test of catalytical activity*

Solutions of various $[(Pyr)_nCuX]_4O_2$, $n=1$ or 2 and X = Cl, Br or I, complexes in methylene chloride were added to separate samples of a 100-fold excess of 2,6-dimethylphenol in methylene chloride. Dioxygen was then bubbled through each solution for 20 min. The product 3,3′,5,5′-tetramethyl-4,4′-diphenoquinone (DPQ) was identified by comparison with an authentic sample ($\lambda_{max} = 431$ nm, $\epsilon = (5.05 \pm 0.01) \times 10^4$ M^{-1} cm^{-1}) [13] as the only product in all cases, equation (4).



(4)

On leaving the above reactions for three days, the yields of (DPQ) varied in the range 36 ± 4%.

4. Conclusion

The oxidation of tetranuclear copper(I) complexes $[(Pyr)_nCuX]_4$ by dioxygen to form $[(Pyr)_nCuX]_4O_2$, which can be isolated as dry stable solids and their reactivity as oxidative coupling catalyts, equation (4), as well as their reaction with CO_2 to form the carbonato-analogs [32], depend on the following points:

(a) Pyrrolidine ligands: pyrrolidene is more basic ($pK_b = 2.73$) than piperidine [6], which affects catalytical activity by increasing the basicity of the oxo groups in $[(Pyr)_nCuX]_4O_2$. The pyrrolidyl hydrogen allows association of the tetranuclear copper(I) with the incoming dioxygen. Such association is key for oxidation of $[(Pyr)_nCuI]_4$ under mild condition, which is not observed for pyridine [33] and *N*,*N*-diethylnicotinamide [34], both of which are less basic and without a N–H.

(b) The haloligands: The structures of $[(Pyr)_nCuX]_4O_2$ are a tetranuclear cubane for X = Cl and Br and a tetranuclear step structure for X = I, scheme 1, predicted from their spectroscopic properties.

(c) The oxo-centers: Basicity of oxo-centers in $[(Pyr)_nCuX]_4O_2$ is the key for the phenolic oxidative coupling process, equation (4). Such basicity is increased as the Cu–O–Cu angle becomes non-linear to localize the free lone pairs on the oxo centers. The degree of non-linearity of Cu–O–Cu was enough to make the oxo center basic for the oxidative coupling process and at the same time permit the addition of CO_2 on the oxo center to form carbonato bridges like $[(Pip)_nCuX]_4(CO_3)_2$ [6, 32].

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