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Properties and reactions of tetranuclear copper(I) complexes $[LCuX]_4$ (L = *N*, *N*-dimethylaminomethylferrocene; X = Cl and Br). Crystal and molecular structure of $(\mu_4\text{-O})L_4Cu_4Cl_6$

Mohamed A. **El-Sayed***
Department of Chemistry Faculty of Science, Alexandria University Alexandria (Egypt)

Adnan Ali**, Geoffrey Davies*
Department of Chemistry, Northeustem University, Boston, MA 02115 (USA)

Scott **Larsen**† and Jon **Zubieta***
Department of Chemistry, Syracuse University, Syracuse, NY I3210 (USA)

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Abstract

Copper(I) chloride and bromide react with equimolar L = *N,N*-dimethylaminomethylferrocene in methylene chloride or nitrobenzene at room temperature under N_2 to give soluble tetranuclear copper(I) complexes $[LCuX]_4$ (VII). The room temperature electronic spectra of L and **VII** are very similar, indicating little, if any, electronic coupling of copper(I) with the ferrocene moiety. Products $[CuX]_4$ completely reduce O_2 to coordinated oxide in the tetranuclear oxocopper(II) products $[LCuX]_4O_2$ (VIII) that are converted by excess CO, to tetranuclear dicarbonatocopper(II) complexes $[LCuX]_4(CO_3)_2$ (IX). VII are oxidized by O_2 to **VIII** in a second-order reaction whose rate-determining step is insertion of 0, through the halo core of **VII.** The properties of **VIII** are consistent with a $(\mu\text{-O})_2[LCuX]_4$ molecular core structure. The electrochemistry of L is not much affected by coordination to copper(I) or copper(H). Attempted crystallization of VIII and **IX** (X=Cl) gives $(\mu_4\text{-O})L_4Cu_4Cl_6$ (Xa), which crystallizes in the tetragonal space group $P\bar{4}2_1c$, with a = 16.930(6), c = 13.084(7) Å, V= 3750 Å^3 and Z= 2. The crystallographic data from 1744 reflections at 233 K were refined to give $R = 0.047$ and R_w = 0.052. The core molecular structure of **Xa** consists of a central oxo group that is tetrahedrally coordinated to four copper(II) centers. Each copper(II) carries a monodentate ligand L and is bridged to three other copper(H) centers by chlorine ligands. This core structure is very similar to those of the *N,N*-diethylnicotinamide and pyridine analogues. Complexes VIII-X are not transmetalated at practical rates by $Co(NS)_2$ and $Ni(NS)_2$ (NS is monoanionic *S*-methyl isopropylidenecarbodithioate). Likely reasons are that steric effects interfere with reaction precursor formation and that VIII-X contain very strong copper-L bonds.

Introduction

The copper(I)/copper(II) couple is a versatile and widespread catalyst for 0, reactions [1–3] but its mechanisms of action are not as well understood as those of metals like iron and cobalt [4].

Many copper-catalyzed reactions depend on prior reduction of O_2 by copper(I) [2–4]. Biomimetic copper(I) dimers reduce 0, in aprotic solvents near -80 °C to give copper(II) complexes with chemically different peroxo bridge geometries [4, 5]. Kinetic measurements of peroxo complex formation, dissociation and intramolecular oxygenase transformation have been made [6]. Peroxocopper complexes that simulate the functions of copper metalloenzymes like hemocyanins and tyrosinases under ambient conditions are being sought [5].

Our work is focussed on simpler industrial copper-ligand catalysts [2]. Cubanes $[pyCuX]_4$ and $[NCuX]_4$ self-assemble when copper(I) halides CuX (X = Cl or Br) are added to equimolar pyridine (py) or monodentate *N*,*N*-diethylnicotinamide (N) in ambient aprotic solvents under N,. They consist of a tetrahedron of halogen atoms with a four-coordinate copper(I) center in each tetrahedral hole [7–9]. Cubanes I and III rapidly and completely reduce 0, to coordinate oxide in tetranuclear oxocopper(II) products $[pyCuX]_4O_2$ (II) and $[NCuX]_4O_2$ (IV), respectively, eqns. (1) and (2) [8–11].

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*Authors to whom correspondence should be addressed.

**On leave of absence from the College of Science and Technology, Abu-Deis, West Bank.

‘On leave of absence from the Materials Technology Division, Johnson Matthey Corporation, 1401 King Road, Westchester, PA 19380, USA.

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$$\underset{\textbf{I}}{[pyCuX]_4} + O_2 \longrightarrow \underset{\textbf{II}}{[pyCuX]_4O_2} \qquad (1)$$

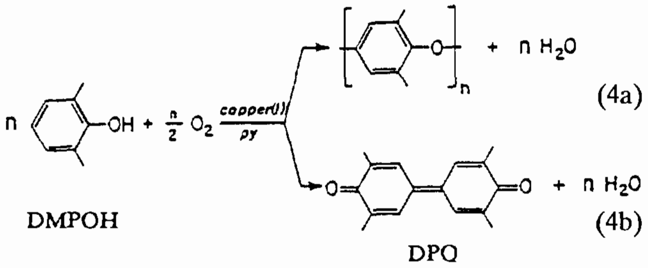
$$\underset{\textbf{III}}{[NCuX]_4} + O_2 \longrightarrow \underset{\textbf{IV}}{[NCuX]_4O_2} \qquad (2)$$

Irreversible reactions (1) and (2) have simple rate law (3), where k_T is the second-order rate constant [8, 9, 11].

$$\text{rate} = k_T[\textbf{I}, \textbf{III}][O_2] \qquad (3)$$

No reaction precursors or intermediates are detected. The enthalpies of activation are small, the entropies of activation are very negative and there is little effect of changing the solvent. This and other evidence [8, 12, 13] indicates rate-determining insertion of O_2 through the halogen atom cores of **I** and **III**. Different product core structures **II** and **IV** result from the point of insertion where the third electron is transferred from copper(I) to O_2 to break the O–O bond [8–13].

Solutions of **I** and **II** initiate and catalyze the ambient oxidative coupling of 2,6-dimethylphenol (DMPOH) to the corresponding diphenoquinone DPQ by O_2, eqn. (4b) [2, 8, 11]. The rate-determining catalytic step is decomposition of the complex (μ_4-O)$py_3Cu_4Cl_4(ODMP)_2$ formed by reaction of DMPOH with the especially basic terminal oxo group of **II** [11].



Products **IV** differ from **II** by undergoing reaction (5) [7–11].

$$\underset{\textbf{IV}}{[NCuX]_4O_2} + 2CO_2 \longrightarrow \underset{\textbf{V}}{[NCuX]_4(CO_3)_2} \qquad (5)$$

Neither **IV** nor **V** initiate reactions (4), but treatment with hard ligand *N*,*N*,*N*′,*N*′-tetraethylethylenediamine (TEED) gives known dimers $(TEED)_2Cu_2X_2O$ and $(TEED)_2Cu_2X_2CO_3$ [14] that catalyze reaction (4a) [15].

Products **II**, **IV** and **V** disproportionate on attempted crystallization to give catalytically inactive crystalline tetramers (μ_4-O)(py, N)$_4Cu_4X_6$ (**VI**) [8, 16].

The use of ferrocene derivatives as large ligands for copper enables us to find out if substantial steric or bonding differences alter the rates of copper(I) oxidation by O_2, if the oxidation products can be crystallized intact and are electrochemically active and if ferrocene–copper targets can be transmetalated [9, 12, 13, 16, 17] to give heteropolymetallic families containing ferrocene.

This paper provides answers to the following questions.

(1) Does hard secondary amine *N*,*N*-dimethylaminomethylferrocene, $L = FcCH_2NMe_2$, react with equimolar copper(I) halides to form cubanes $[LCuX]_4$ (**VII**) or dimers $L_2Cu_2X_2$?

(2) Are **VII** oxidized to $[LCuX]_4O_2$ (**VIII**) by O_2 and is iron(II) in L also oxidized? How do the oxidation rates of **I**, **III** and **VII** compare? What is the rate-determining step? Do products **VIII** react with CO_2 to give tetranuclear $[LCuX]_4(CO_3)_2$ (**IX**)? Can **VIII** and **IX** be crystallized or do they disproportionate to (μ_4-O)$L_4Cu_4X_6$ (**X**)?

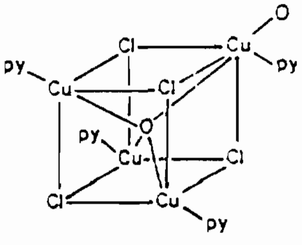
(3) How do the spectral and other properties of **II** and **IV–X** compare? Are **VIII–X** electrochemically active? Do they initiate reactions (4)?

(4) Complexes **I–VI** are stoichiometrically transmetalated by $M(NS)_n$ reagents to give a wide variety of new heteropolymetallic products. Here M is Fe, Co, Ni, Cu, Zn, Cd, Hg or Sn and NS is a monoanionic *S*-methyl hydrazinecarbodithioate ligand [9, 17]. Are **VII–X** transmetalated by $M(NS)_n$ reagents at practical rates? If not, why not?

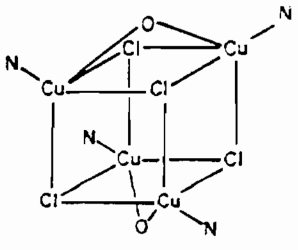
Experimental

Materials

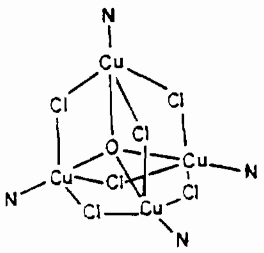
Nitrobenzene was distilled under reduced pressure from P_2O_5 and stored over 4 Å molecular sieves. Methylene chloride was purified as described previously



II



IV



VI

[7]. High purity N_2 was deoxygenated by passage through a column of Alfa DE-OX solid catalyst. Copper(I) halides CuX were prepared as described in the literature [18]. *N*,*N*-dimethylaminomethylferrocene (L: Strem) and tetrabutylammonium perchlorate (TBAP: Eastman polarographic grade) were used as received.

Synthesis of tetranuclear copper(I) complexes $[LCuX]_4$ (X=Cl (VIIa) and Br (VIIb))

Solid CuX (1.0 mmol) was added to a deoxygenated solution of L (1.0 mmol) in methylene chloride (30 ml) and the mixture was stirred at room temperature under N_2 until a clear solution of **VIIa** or **VIIb** was obtained. These products are very air-sensitive and the solids isolated by vacuum solvent evaporation gave irreproducible elemental analytical data. However, cryoscopic measurements established that **VIIa** and **VIIb** are tetranuclear in nitrobenzene (Table 1).

Synthesis of tetranuclear copper(II) complexes $[LCuX]_4O_2$ (X=Cl (VIIIa) and Br (VIIIb)) and $[LCuX]_4(CO_3)_2$ (X= Cl (IXa) and Br (IXb))

Brown solutions of tetranuclear complexes $[LCuCl]_4O_2$ and $[LCuBr]_4O_2$ (**VIIIa** and **VIIIb**, respectively) resulted from treatment of **VIIa** and **VIIb** in methylene chloride or nitrobenzene with flowing 0, at room temperature for 20 min. The stoichiometry of reaction (6) was determined from manometric 0, uptake data with a standard Warburg apparatus at 25 °C [7].

$$\mathbf{VII} + O_2 \longrightarrow \mathbf{VIII} \qquad (6)$$

Solid products **VIIIa** and **VIIIb** were isolated from solution by solvent evaporation or were reacted in solution with excess CO, to give solid tetranuclear products $[LCuCl]_4(CO_3)_2$ (**IXa**) and $[LCuBr]_4(CO_3)_2$ (**IXb**), respectively, eqn. (7), after solvent evaporation [7, 8].

$$\text{VIII} + 2CO_2 \longrightarrow \text{IX} \qquad (7)$$

Attempted crystallization of **VIIIa** and **IXa** gave $(\mu_4\text{-}O)L_4Cu_4Cl_6$ (Xa) whose crystal and molecular structure is described below. Analytical and cryoscopic molecular weight data are given in Table 1.

Spectral and electrochemical measurements

The electronic spectra of VII-X in methylene chloride or nitrobenzene were measured under N_2 with Perkin-Elmer Lambda 4B and Beckman DK-1A spectrophotometers in matched quartz cells at room temperature. EPR spectra of 5.0 mM solutions of WI and IX in methylene chloride were recorded at 100 kHz and 6.28 G modulation amplitude on a Bruker Electrospin model ESP 300 spectrometer. Incident power was 100 mW. Resonance conditions were found at *ca.* 9.39 GHz (X-band) at room temperature and 130 K. Cyclic voltammograms were recorded with a Bioanalytical Systems CV-1B instrument connected to a Honeywell model 530 X-Y recorder. No IR compensation was employed. A platinum working electrode (Beckman) and a platinum wire auxiliary electrode were employed in all measurements. Samples VIII and IX were dissolved in deoxygenated methylene chloride containing 0.1 M TBAP as the supporting electrolyte. All solutions were kept under N_2 during electrochemical measurements. All potentials were measured with respect to a saturated calomel electrode (SCE) and referenced to the potential of the ferrocenium/ferrocene couple (0.40 V) [19].

TABLE 1. Analytical and cryoscopic data for products $[LCuX]_4$ and $[LCuX]_4Y_2$ (Y=O and CO_3)

Label	X, Y	Anal.“* ^{b} (%)					M_r^{c}
		C	H	N	CU	Fe	
VIIa	cl						1350 ± 20 (1368)
VIIb	Br						1440 ± 20 (1458)
VIIIa	Cl, O	44.4 (44.6)	4.5 (4.9)	3.7 (4.0)	18.5 (18.1)	16.3 (16.0)	1330 ± 20 (1400)
VIIIb	Br, 0	43.5 (43.5)	4.8 (4.6)	3.9 (3.8)	16.9 (17.1)	14.9 (15.1)	1420 ± 30 (1490)
M a	Cl, co,	39.6 (395)	3.9 (4.3)	3.1 (3.5)	16.5 (16.1)	13.8 (14.2)	1490 ± 30 (1580)
IXb	Br, CO_3	38.8 (38.9)	3.8 (4.1)	3.3 (3.4)	15.1 (15.2)	13.3 (13.4)	1550 ± 30 (1660)

“Calculated values in parentheses. “Solid complexes VII are too air-sensitive to give reproducible elemental analytical data. See text. ‘Measured in nitrobenzene at the 3-5X 10^{-2} molal level [7].

TABLE 2. X-ray data for the structural determination of $(\mu_4\text{-O})L_4Cu_4Cl_6$ (Xa)

Formula weight	1787.0
a (Å)	16.930(6)
c (Å)	13.084(7)
V (Å^3)	3750(2)
Z	2
Space group	$P\bar{4}2_1c$
D_{calc} (g cm^{-3})	1582
μ(Mo Kα) (cm^{-1})	24.09
No. reflections	1744
R	0.047
R_w	0.052
Goodness of fit	1.48

TABLE 3. Atomic coordinates (X 10’) and equivalent isotropic displacement coefficients (Å^2 x 10^4)

	x	Y	z	U_{eq}[a]
Cu(1)	515(1)	766(1)	854(1)	255(4)
Fe(1)	2569(1)	3656(1)	1337(1)	382(6)
Cl(1)	−290(2)	1716(2)	−32(3)	420(11)
Cl(2)	0	0	2234(3)	480(17)
O(1)	0	0	0	203(37)
N(8)	1040(6)	1548(6)	1815(7)	305(32)
C(1)	2609(12)	3507(11)	−169(11)	723(71)
C(2)	3411(10)	3549(12)	225(12)	680(69)
C(3)	3447(11)	4297(11)	626(11)	668(67)
C(4)	2732(12)	4702(10)	564(13)	758(74)
C(5)	2216(12)	4224(12)	73(11)	765(74)
C(6)	1611(9)	3499(8)	2269(11)	523(52)
C(7)	2217(11)	3889(10)	2820(11)	588(58)
C(8)	2889(11)	3419(10)	2844(12)	634(65)
C(9)	2694(8)	2698(8)	2296(11)	447(48)
C(10)	1929(8)	2746(7)	1909(10)	379(45)
C(11)	1476(8)	2152(7)	1228(8)	325(39)
C(12)	415(8)	1942(8)	2437(9)	422(45)
C(13)	1604(9)	1091(8)	2503(9)	451(48)
Cl(3)	9159	4024	1429	4610(123)
Cl(4)	9056	3968	−882	5277(148)
C(20)	9473	3885	84	3164(269)

[a]Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

Determination of the crystal and molecular structure of $(\mu_4\text{-O})L_4Cu_4Cl_6$ (Xa)

Attempted crystallization of VIIIa and IXa from ethylene chloride/diethyl ether gave single crystals of Xa that were suitable for an X-ray structural determination. Crystal data are presented in Table 2. Atomic positional parameters and selected bond distances and angles are listed in Tables 3 and 4, respectively. Full details of the data collection methods and refinement procedures are given in ref. 20. See also ‘Supplementary material’.

Data were collected on a Nicolet R3m/V diffractometer at 233 K. Solution and refinement of the structure was carried out using the SHELXTL programs provided by Seimans Corporation. Neutral atom-scattering factors were used throughout and no extinction correction was applied. The structure was solved using direct methods and refined by full-matrix least-squares. The final difference Fourier map revealed the presence of a highly disordered methylene chloride molecule of crystallization. No suitable disorder model based on partial occupancies could be developed. The expedient of locating the carbon and chlorine atoms at the major peak position produced a model which accounted for the residual electron density but which gave large isotropic temperature factors. Since the molecule Xa was well-behaved, no further attempt to model the disorder was made. With the exception of the hydrogen atoms and the atoms of the solvent molecule, all atoms were refined anisotropically. Calculated hydrogen atom positions were used in the final refinement phase.

Kinetic measurements

The rates of reactions (6) in nitrobenzene were measured by monitoring absorbance increases as a function of time at fixed wavelength in the region 750–850 nm in a Hi-Tech Scientific model SFL41 stopped-flow spectrophotometer [21] with VII in pseudo-first-order excess. The total reactant concentration range was $[\mathrm{VII}]_0 = 35.2\text{–}141$ mM, with $[O_2]_0 = 0.22$ mM. Temperature was controlled to ±0.05 °C in the range 18.0–47.0 °C. Pseudo-first-order rate constants k_{obs} were obtained from the slopes of linear plots of $\log(A_\infty - A_t)$ versus time, where A_t is the absorbance at fixed wavelength and temperature at time t. Each run was repeated at least three times under fixed experimental conditions to establish an upper limit of ±4% for each reported rate constant.

The inactivity of complexes VI-X as initiators for reactions (4) was confirmed under standard conditions at room temperature [8].

Results and discussion

Copper(I) halides CuX (X=Cl and Br) react with equimolar *N,N*-dimethylaminomethylferrocene, L, in ambient methylene chloride and nitrobenzene under N_2 to give very air-sensitive solutions of tetranuclear complexes $[LCuX]_4$. As found with py [8, 11], N [8] and *N,N,N′,N′*-tetraalkyldiamine [14, 15] ligands, attempted isolation of the solid copper(I) products resulted in air-oxidation and irreproducible elemental analyses. However, cryoscopic measurements in nitrobenzene under N_2 (Table 1) show that the products are tetramers VIIa and VIIb and not dimers $L_2Cu_2X_2$. This is reasonable because dihalo-bridged dimers LCu(X,X)CuL would contain three-coordinate metal centers, which are rare for copper(I) complexes [9].

TABLE 4. Selected bond lengths (Å) and angles (°) for $(\mu_4\text{-O})L_4Cu_4Cl_6$ (Xa)

Cu(1)–Cl(1)	2.407(4)	Cu(1)–Cl(2)	2.387(4)
Cu(1)–O(1)	1.921(2)	Cu(1)–N(8)	2.032(10)
Cu(1)–Cl(1A)	2.437(4)	Fe(1)–C(1)	1.988(14)
Fe(1)–C(2)	2.046(17)	Fe(1)–C(3)	2.063(18)
Fe(1)–C(4)	2.059(17)	Fe(1)–C(5)	2.004(17)
Fe(1)–C(6)	2.045(15)	Fe(1)–C(7)	2.067(15)
Fe(1)–C(8)	2.083(16)	Fe(1)–C(9)	2.061(14)
Fe(1)–C(10)	2.025(13)	Cl(1)–Cu(1A)	2.437(4)
Cl(2)–Cu(1B)	2.387(4)	O(1)–Cu(1A)	1.921(2)
O(1)–Cu(1B)	1.921(2)	O(1)–Cu(1C)	1.921(2)
N(8)–C(11)	1.476(15)	N(8)–C(12)	1.493(16)
N(8)–C(13)	1.524(17)	C(1)–C(2)	1.455(26)
C(1)–C(5)	1.419(28)	C(2)–C(3)	1.371(26)
C(3)–C(4)	1.395(28)	C(4)–C(5)	1.353(27)
C(6)–C(7)	1.418(22)	C(6)–C(10)	1.461(19)
C(7)–C(8)	1.389(25)	C(8)–C(9)	1.453(22)
C(9)–C(10)	1.393(19)	C(10)–C(11)	1.547(17)
Cl(1)–Cu(1)–Cl(2)	121.4(1)	Cl(1)–Cu(1)–O(1)	85.0(1)
Cl(2)–Cu(1)–O(1)	84.7(1)	Cl(1)–Cu(1)–N(8)	96.3(3)
Cl(2)–Cu(1)–N(8)	92.7(3)	O(1)–Cu(1)–N(8)	177.4(3)
Cl(1)–Cu(1)–Cl(1A)	118.7(1)	Cl(2)–Cu(1)–Cl(1A)	117.3(1 j
O(1)–Cu(1)–Cl(1A)	84.2(1)	N(8)–Cu(1)–Cl(1A)	97.1(3)
		Cu(1)–Cl(1)–Cu(1A)	80.9(1)
Cu(1)–Cl(2)–Cu(1B)	81.8(2)	Cu(1)–O(1)–Cu(1A)	109.8(1)
Cu(1)–O(1)–Cu(1B)	108.8(1)	Cu(1A)–O(1)–Cu(1B)	109.8(1)
Cu(1)–O(1)–Cu(1C)	109.8(1)	Cu(1A)–O(1)–Cu(1C)	108.8(1)
Cu(1B)–O(1)–Cu(1C)	109.8(1)	Cu(1)–N(8)–C(11)	110.4(7)
Cu(1)–N(8)–C(12)	108.5(7)		
Cu(1)–N(8)–C(13)	107.9(7)		

Other hard amine ligands form tetramers with copper(I) halides under similar conditions [22].

Electronic spectra of VII

The electronic spectra of L (Fig. 1), **VIIa** and **VIIb** are virtually identical in methylene chloride. This indicates that the copper(I) centers of VII are nearly transparent in the 550-900 nm region. There is little, if any, electronic coupling between copper(I) and the iron(II) of coordinated L at room temperature, presumably because of the intervening methylene group. By contrast, the ligand 4-pyridylferrocene responds electrochemically to changes in a metal center to which it is attached [23].

Stoichiometry of oxidation of VII by O_2

Manometric O_2 uptake measurements in nitrobenzene at room temperature and the data in Table 1 show that tetranuclear complexes **VIIa** and **VIIb** completely reduce O_2 to give tetranuclear oxocopper(II) products **VIIIa** and **VIIIb**, respectively, eqn. (6). Exposure of solutions of **VIIIa** and **VIIIb** to O_2 for up to two weeks gave no manometric evidence for oxidation of the ferrocene ligand L. Oxidative stability of the a-methyl group and iron(II) center of L is notable: *N,N,N′,N′*-tetraalkyldiamines and alkylated pyridines undergo slow oxidative degradation when coordinated to oxocopper(II) centers [14]. Iron(II) centers in transmetalation products like $N_4Cu_3Fe(NS)_2X_4$ and $N_4CuFeCl_4$ also are air-sensitive [24]. Oxidative stability of coordinated L supports an 'insertion' [8] oxidation mechanism for reactions (6), with no partially reduced oxygen species available to oxidize iron(II) in L (see below).

Reaction of VZII with CO,

Products **VIIIa** and **VIIIb** react with excess CO, as in eqn. (7), indicating that they contain equivalent μ-oxo groups in opposite faces of a cubane, as in core structure IV with L replacing N [8, 10]. Similar core structures for IV, **VIII** and **V**, **IX** also are indicated by their inability to initiate reactions (4) in methylene chloride at room temperature [7–11].

Electronic spectra of VIII and IX

Ligand L does not significantly absorb light in the 550-900 nm region (Fig. 1). The near-IR electronic spectra of IV and **VIII** (Fig. 1) and **V** and IX (Fig. 2) are comparable and indicate copper(II) centers coordinated by three halo ligands, an oxo group and L in a molecular cubane structure [9, 25]. Complexes $[NCuX]_4Y_2$ (X= Cl or Br; Y=O or CO,) and their partially transmetalated derivatives commonly have ab-

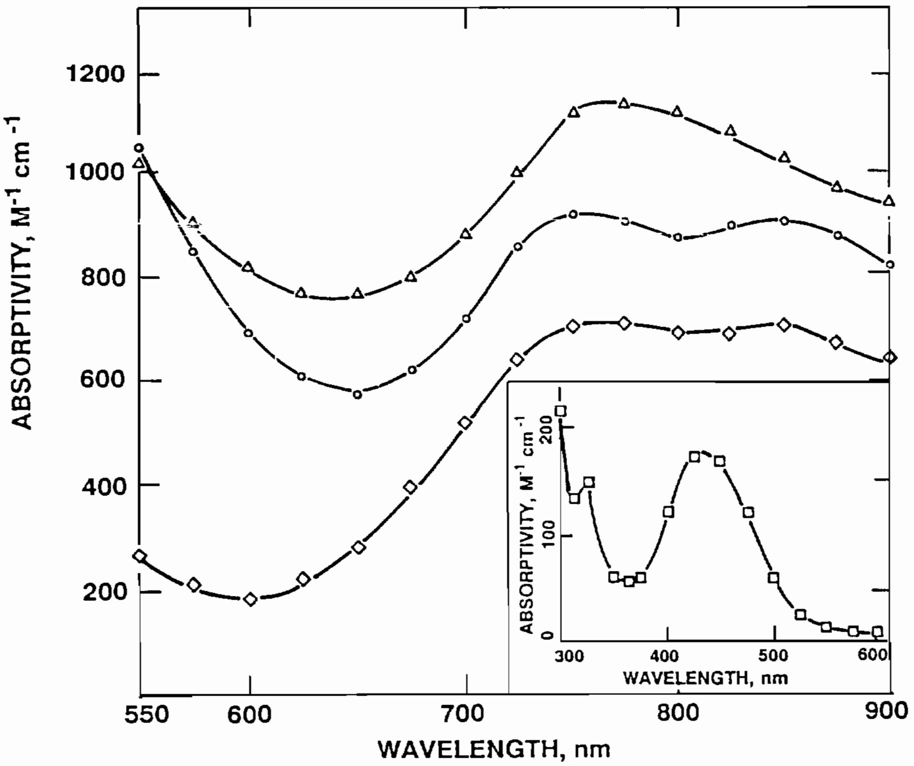


Fig. 1. Electronic spectra of **VIIIa** (○), **VIIIb** (△) and $[NCuCl]_4O_2$ (**IVa**) [8, 9] (◇) in methylene chloride at 25 °C. Inset: spectrum of L.

sorption minima near 600 nm [10, 16], but minima are observed at longer wavelength with ligand L (Figs. 1 and 2). Ligand L intensifies the copper(II) spectra except in $[LCuBr]_4(CO_3)_2$ (**IXb**), whose maximum molar absorptivities are unexpectedly low (Fig. 2).

The electronic spectrum of polar pyridinecopper(II) complex **II** is intensified by changing the solvent from methylene chloride to nitrobenzene [10] but no such effect is observed with **IV–VI**. No solvent spectral difference was found for **VIII**. This is another indication that **VIII** are analogues of core structure **IV** [10].

EPR spectra of L, VIII and IX

Ligand L displays an isotropic EPR spectrum in methylene chloride at 300 K (Fig. 3). The room temperature EPR spectra of **VIII** and **IX** contain signals from iron(II) and copper(II) near $g = 2$ (Fig. 3). Products **VIII** and **IX** are EPR active at 130 K, where L is EPR silent (Fig. 4). The EPR spectra of **VIII** are axial (Table 5), indicating a square pyramidal geometry about copper(II) [14b, 26]. The EPR spectrum of **IXa** is rhombic, indicating a trigonal pyramidal geometry about copper(II) [14b, 26]. These properties are consistent with those of **IV** and **V** [10, 27] and indicate the same respective core structures.

Attempted crystallization of VIII and IX

Complexes **II**, **IV** and **V** disproportionate [8, 10] to give crystalline $(\mu_4\text{-O})(py,N)_4CuX_6$ [16] on attempted crystallization. Attempts to crystallize **VIIIa** and **IXa** from methylene chloride and nitrobenzene by a variety of techniques gave $(\mu_4\text{-O})L_4Cu_4Cl_6$ (**Xa**) as the only crystalline product. The best single crystals were obtained by room temperature diethyl ether diffusion into methylene chloride solutions of **IXa**. The electronic spectrum of **Xa** in methylene chloride is less intense than that of the *N*,*N*-diethylnicotinamide analogue and has an absorption minimum near 650 nm (Fig. 5).

The molecular structure of $(\mu_4\text{-O})L_4Cu_4Cl_6$ (Xa)

As illustrated in Fig. 6, the structure of **Xa** consists of $(\mu_4\text{-O})[(C_5H_5)Fe(C_5H_4CH_2NMe_2]_4Cu_4Cl_6$ molecules. The central oxo group of each molecule is constrained to lie on the crystallographic four-fold inversion axis and is tetrahedrally coordinated to four copper(II) centers. The chlorine ligands bridge pairs of copper(II) sites. The coordination sphere about copper centers is trigonal pyramidal $[CuCl_3,O,N]$, with the chlorine donors occupying the equatorial positions and the axial sites defined by the central oxo group and the amine donor group of the $[(C_5H_5)Fe(C_5H_4NMe)_2]$ moiety. The copper atom is displaced 0.17 Å from the Cl_3 plane in the direction of the amine donor.

The metrical parameters for the Cu_4Cl_6O core are similar to those previously reported for other examples of this structural unit [16, 28–31]. The range of Cl–Cu–Cl angles (117.3(1)–121.4(1)°) is close to the idealized limit

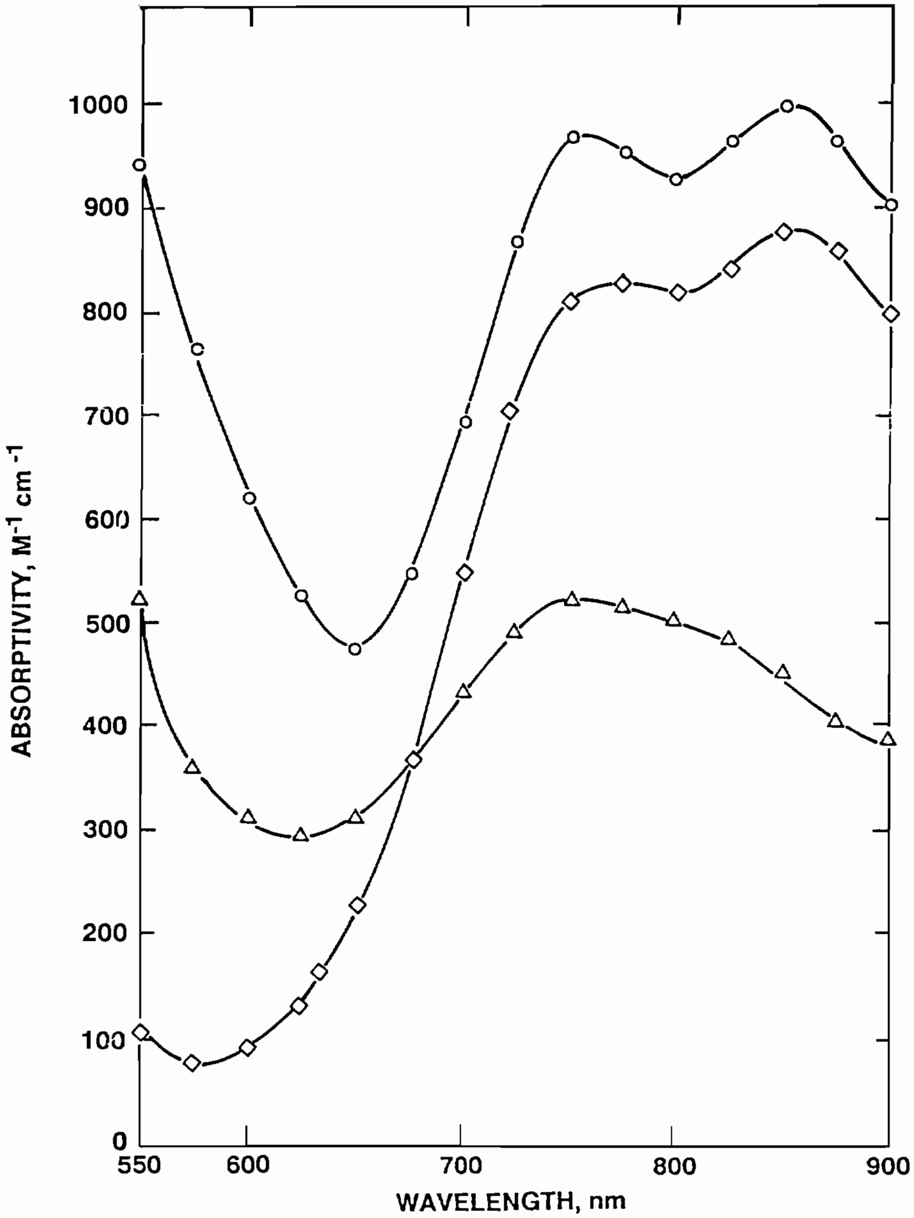


Fig. 2. Electronic spectra of **IXa** (○), **IXb** (△) and $[NCuBr]_4(CO_3)_2$ [8, 9] (◇) in methylene chloride at 25 °C.

of 120° and significantly narrower than that observed for $(\mu_4\text{-O})N_4Cu_4Cl_6$ (104.0–134.6°) [16]. This feature most likely reflects the geometric constraints of the pyridyl nitrogen donor of $(\mu_4\text{-O})N_4Cu_4Cl_6$ relative to the amine nitrogen donor of **Xa**.

The structural parameters associated with the $[(C_5H_5)Fe(C_5H_4CH_2NMe_2)]$ unit are unexceptional. The average Fe–C distance is 2.04(2) Å, with a range of 1.99(1)–2.08(2) Å.

Kinetics of oxidation of I, III and VII by O_2 in nitrobenzene

The reactions of excess copper(I) complexes **VII** with O_2 result in large absorption increases in the 750–850 nm that are easily monitored by stopped-flow spectrophotometry. Plots of $\ln(A_\infty - A_t)$ were linear for at least five half-lives under all experimental conditions, indicating a first-order dependence of the rate on $[O_2]$. Plots of the pseudo-first-order rate constant k_{obs} versus $[VII]_0$ were linear and passed through the origin (Fig. 7), indicating irreversible reaction (6) with second-order rate law (3) and no detectable intermediates. The kinetic data are collected in Table 6. There was no kinetic evidence for oxidation of iron(II) in ligand L. This confirms the manometric measurements and strongly suggests that no reduced oxygen species (superoxide, peroxide or O^-) are available to oxidize iron(II) in L.

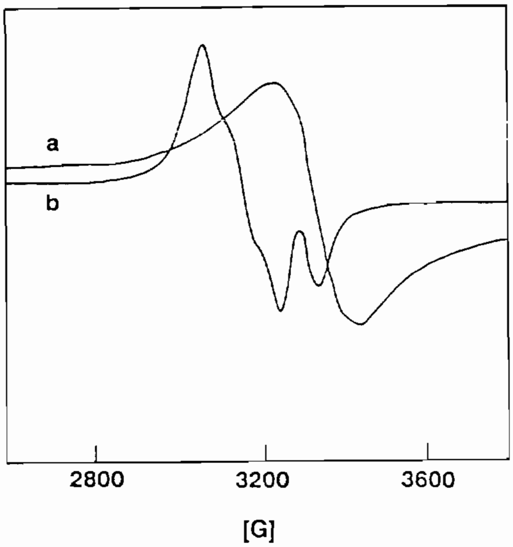


Fig. 3. EPR spectra of L (a) and **VIIIa** (b) in methylene chloride at 300 K. Concentration 5 mM. Gain 8×10^4.

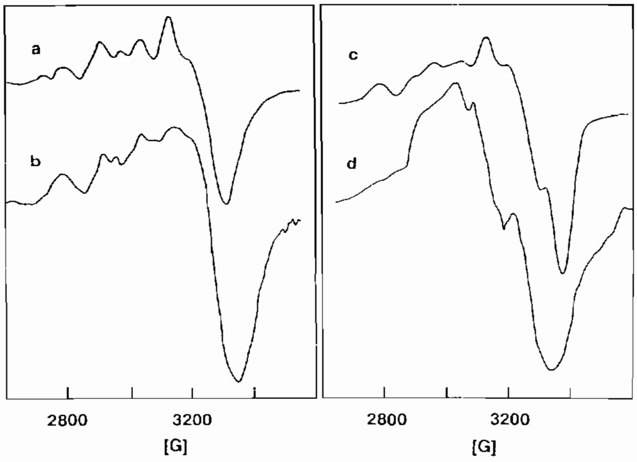


Fig. 4. EPR spectra in methylene chloride at 130 K: (a) **VIIIa**; (b) **VIIIb**; (c) **IXa**; (d) **IXb**. Concentration 5 mM. Gain 1×10^3.

Transmetalation of $[NCuX]_4$ with equimolar $M(NS)_2$ and $Co(NS)_3$ reagents gives $N_3Cu_3M(NS)X_4$ and $N_3Cu_3Co(NS)_2X_4$ products that contain three and two copper(I) centers, respectively. Reduction of O_2 by these copper(I) centers gives reduced oxygen species that oxidize coordinated NS to the corresponding disulfide [12, 13]. The iron(II) in ferrocenes is oxidized by radiolytically generated radicals [32], so reduced oxygen species that escaped from the cores of $[LCuX]_4/O_2$ systems would more than likely oxidize the iron(II) center of L.

Tetranuclear copper(I) complexes $[(py,N)CuX]_4$ are oxidized by O_2 with second-order rate law (3) [8, 11], while copper(I) dimers like $py_4Cu_2Cl_2$ [8] and $(TEED)_2Cu_2X_2$ (X = Cl or Br) [14, 15] characteristically have a third-order oxidation rate law. Second-order behavior in the present study is consistent with the cryoscopic evidence for tetranuclear copper(I) reactants in Table 1.

Second-order rate constants k_T (Table 6) are similar to those for oxidation of $[(N,py)CuCl]_4$ complexes (Table 7), indicating no coordinative interference from ligand L in reaction (6). Changing X from Cl to Br in $[NCuX]_4$ results in a substantial decrease in k_T, largely because of an increase in the activation enthalpy (Table 7) [8]. However, the oxidation rate decreases only slightly when X in $[LCuX]_4$ is changed from Cl to Br, indicating that coordination of hard ligand L to copper(I) loosens the halo core and facilitates O_2 insertion. The same effect occurs on increasing the coordination number of copper(I) in $[(py,N)_mCuCl]_4$ from four to five [8, 11]. The activation parameters for reactions (6) fit the correlation in Fig. 6 of ref. 14b, indicating a common insertion mechanism for the oxidation of $[(L,py,N)CuX]_4$ complexes by O_2.

Electrochemical measurements

Ligand L and complexes $[LCuCl]_4Y_2$ (Y = O or CO_3) exhibit quasi-reversible cyclic voltammograms in room-temperature methylene chloride (Fig. 8 and Table 8). The E^f values indicate that coordination of L to copper in **VII–IX** has little effect on its electrochemistry [23], although $|E|$ for **VIIIa** is notably smaller than for L and **IXa** (Table 8).

Attempted transmetalation of VII–X

Complexes **VIII**, **IX** and **X** are very slowly (if at all) transmetalated by $Co(NS)_2$ and $Ni(NS)_2$ (NS is monanionic *S*-methyl isopropylidenecarbodiothioate), which are excellent stoichiometric transmetalators of targets **I–VI** in aprotic solvents (for example, see eqn. (8)) [12, 13, 16, 17, 33a]. This is unfortunate because successful transmetalation would provide the first examples of heteropolymetallic molecular families containing metalated ligands.

$$\textbf{VIa} + xNi(NS)_2 \longrightarrow (\mu_4\text{-}O)N_4Cu_{4-x}Ni_xCl_6 + xCu(NS)_2 \quad (8)$$

We are exploring the possibility that 4-pyridylferrocene, L′ [23], gives transmetalatable analogues of **VII–X**.

The very low transmetalation rates for targets **VIII–X** could be due to steric effects: transmetalation reactions proceed through precursors formed by sharing of nucleophilic target and transmetalator donor atoms [17, 33]. A bulky ligand like L could interfere with this requirement. Steric effects and copper–ligand bond strengths are not deciding factors in reactions (1), (2) and (6) because coordination of O_2 to copper(I) is not involved in the rate-determining step [8, 11, 14a]. Evidence for another likely inhibiting factor comes from the different thermal properties of **VIa** and **Xa** [34].

TABLE 5. EPR and electronic spectral data for complexes $[LCuX]_4Y_2$ (Y = O and CO_3) in methylene chloride

Complex	Temperature (K)	EPR[a]							λ_{max} (nm) (E_λ (M^{-1} cm^{-1}))
		$A_\parallel$[b]	$g_\parallel$	$g_\perp$	g_1	g_2	g_3	$\langle g \rangle$	
VIIIa[c]	300								750(920), 850(900)
	130	133	2.27	2.04					
VIIIb[c]	300								775(1120), 850(1020)
	130	133	2.26	2.01					
IXa[c]	300								750(970), 850(1000)
	130				2.26	2.07	2.00	2.11	
IXb[c]	300								770(520), 850(450)
	130				2.24	2.15	2.02	2.14	

[a] Ligand L has an isotropic EPR spectrum at $g_i = 2.22$ at 300 K (Fig. 3) and is inactive at 130 K. [b] Units are 10^{-4} cm^{-1}. [c] EPR spectra at 300 K consist of a combination of copper(II) and iron(II) signals (Fig. 3).

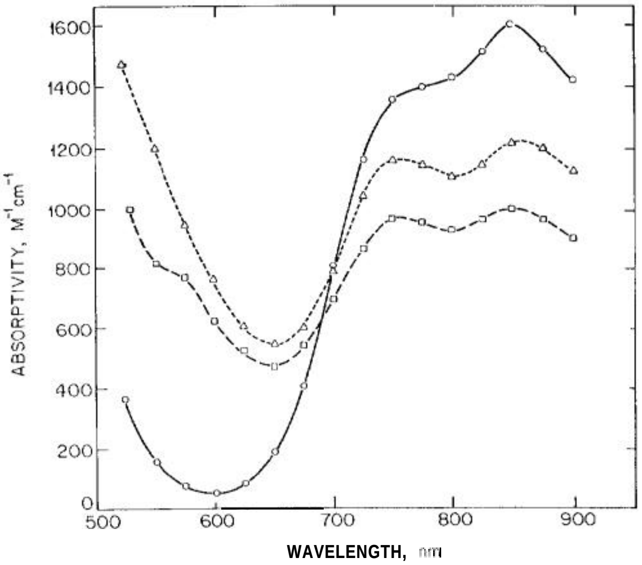


Fig. 5. Electronic spectra of $(\mu_4\text{-}O)N_4Cu_4Cl_6$ (○) [16], $(\mu_4\text{-}O)L_4Cu_4Cl_6$ (△) and $[LCuCl]_4(CO_3)_2$ (□) in methylene chloride at 25 °C.

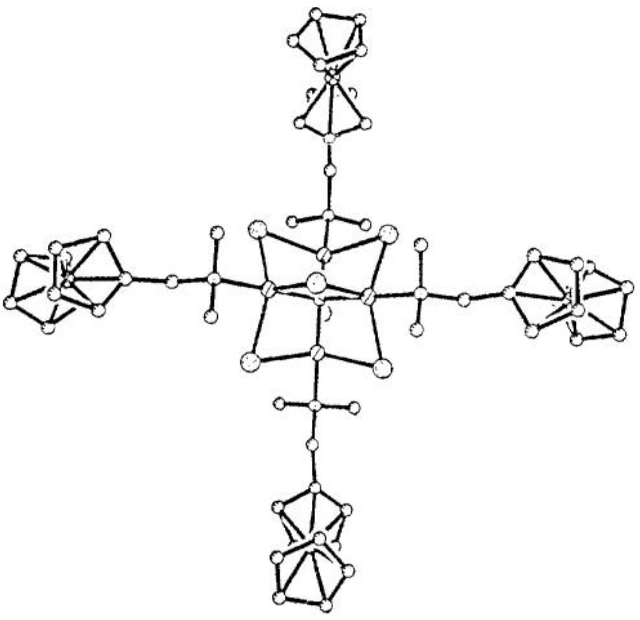


Fig. 6. Molecular structure of $(\mu_4\text{-}O)L_4Cu_4Cl_6$, L = *N,N*-dimethylaminomethylferrocene.

Thermogravimetric experiments show that **Xa** only begins to lose one of its L ligands at c. 230 °C, whereas **VIa** rapidly loses all four of its N ligands at 50 °C [34]. Strong copper-ligand target bonds clearly inhibit metal exchange leading to transmetalation, as confirmed in other systems [17, 21].

Conclusions

Copper(I) chloride and bromide form tetranuclear complexes $[LCuX]_4$ with equimolar L = *N,N*-dimethylaminomethylferrocene. These complexes are very soluble in methylene chloride and nitrobenzene and completely reduce O_2 to coordinate oxide in products $(\mu\text{-}O)_2[LCuX]_4$. The coordinated ligand L is oxidatively stable in products **VIII** despite its iron(II) center and α-methylene group. Insertion of O_2 through the halo cores of $[(L,N,py)CuX]_4$ reductants is the rate-determining oxidation step. Because of their $(\mu\text{-}O)_2[LCuX]_4$ core structure and despite the fact that they contain a hard secondary amine ligand, the products of reactions (6) and (7) do not initiate or catalyze the oxidative coupling of 2,6-dimethylphenol by O_2, eqn. (4). Attempted crystallization of **VIIIa** and **IXa** gives crystalline $(\mu_4\text{-}O)L_4Cu_4Cl_6$ (**Xa**) whose crystal and molecular structures are very similar to those of $(\mu_4\text{-}O)(N,py)_4Cu_4Cl_6$. Complexes **VII**–**Xa** are very poor transmetalation targets, most probably because they contain strong Cu-L bonds.

We still do not fully understand why $[pyCuX]_4$ complexes are oxidized by O_2 to give catalytically active

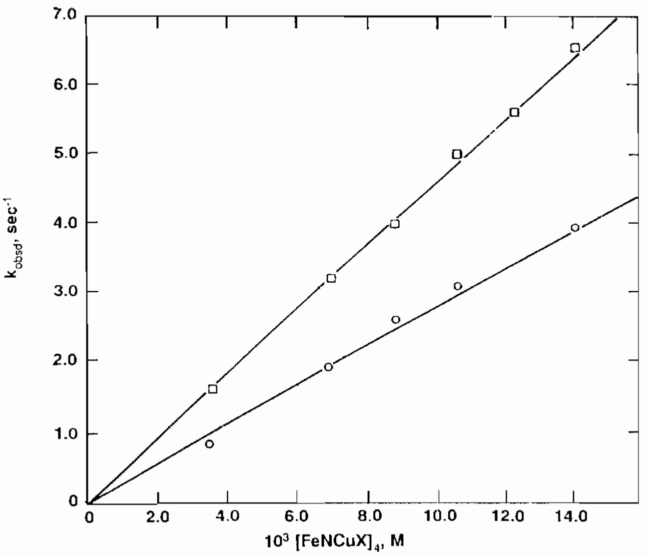


Fig. 7. Second-order plots for the oxidation of $[LCuX]_4$ by O_2 in nitrobenzene: X-Cl (□); X=Br (○). The experimental temperature is 18.0 °C.

TABLE 6. Kinetic data for oxidation of excess $[LCuX]_4$ with O_2 in nitrobenzene[a]

X	Temperature (°C)	k_T[b]	$\Delta H_T^{\ddagger}$[c]	$\Delta S_T^{\ddagger}$[d]
Cl	18.0	45.5	3.4	−39
	25.0	52.6		
	33.3	64.8		
	41.2	69.0		
Br	18.0	29.5	3.1	−41
	25.0	33.9		
	32.7	40.9		
	40.0	43.2		
	47.0	45.4		

[a] $[[LCuX]_4]_0$=35–141 mM; $[O_2]_0$=0.22 mM. [b] Units are M^{-1} s^{-1}. Maximum error is ±4%. [c] Units are kcal mol^{-1}. Typical error is ±0.3 kcal mol^{-1}. [d] Units are cal deg^{-1} mol^{-1} at 25 °C. Typical error is ±3 cal deg^{-1} mol^{-1}.

TABLE 7. Kinetic data for oxidation of complexes $[LCuX]_4$, $[NCuX]_4$ and $[pyCuCl]_4$ with O_2 in nitrobenzene

Complex	k_T[a]	$\Delta H_T^{\ddagger}$[b]	$\Delta S_T^{\ddagger}$[c]	Reference
$[LCuCl]_4$	53	3.4	−39	this work
$[NCuCl]_4$[d]	15	3.9	−40	7
$[pyCuCl]_4$[e]	110	2.1	−58	11
$[LCuBr]_4$	34	3.1	−41	this work
$[NCuBr]_4$[d]	0.6	5.9	−40	7

[a] Units are M^{-1} s^{-1}; maximum error is ±4%. [b] Units are kcal mol^{-1}; typical error is ±0.3 kcal mol^{-1}. [c] Units are cal deg^{-1} mol^{-1} at 25 °C; typical error is ±3 cal deg^{-1} mol^{-1}. [d] N is *N*,*N*-diethylnicotinamide. [e] py is pyridine.

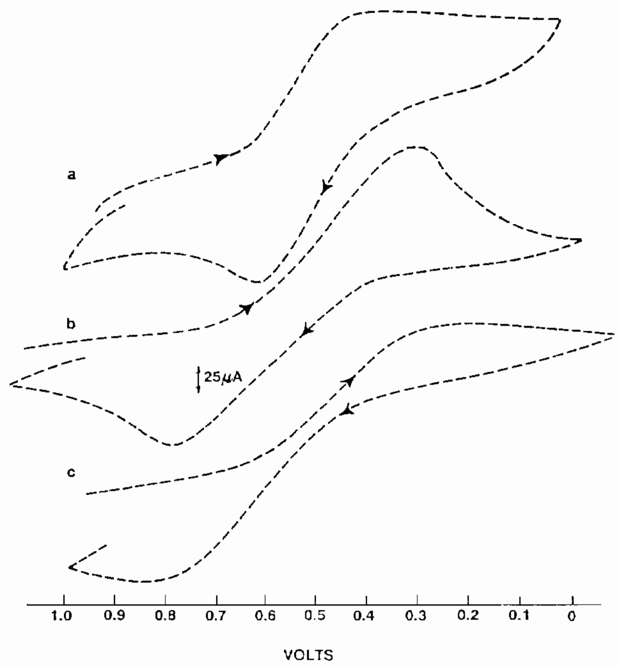


Fig. 8. Cyclic voltammograms for **VIIIa** (a), **IXa** (b) and L (c) in methylene chloride containing 0.1 M TBAP at 25 °C. The scan rate is 200 mV s^{-1}.

TABLE 8. Cyclic voltammetric data for 1.0 mM solutions of L and $[LCuCl]_4Y_2$ (Y = O and CO_3) in methylene chloride containing 0.1 M TBAP[a]

Solute	ν (mV s^{-1})	E^f (V)	$\lvert\Delta E\rvert$ (V)
L	200	0.41	0.40
	150	0.41	0.37
	100	0.41	0.33
	50	0.42	0.29
		av. 0.41	av. 0.35
VIIIa	200	0.41	0.17
	150	0.41	0.17
	100	0.41	0.16
	50	0.38	0.21
		av. 0.40	av. 0.18
IXa	200	0.45	0.47
	150	0.45	0.43
	100	0.45	0.43
	50	0.45	0.29
		av. 0.45	av. 0.40

[a] Calibrated with the ferrocenium/ferrocene couple at 0.40 V vs. SCE [19].

core structure **II** while $[(L,N)CuX]_4$ complexes are oxidized by O_2 to give inactive core structure **IV**. What special property of copper-coordinated py is responsible?

Supplementary material

A structure determination summary and tables showing atomic positional parameters, bond lengths, bond angles, anisotropic displacement coefficients, hydrogen atom coordinates and observed and calculated structure factors are available from J.Z.

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