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Oxidation of tetranuclear copper(I) complexes $[NCuX]_4$ (N = *N,N*-diethylnicotinamide; X = Cl, Br or I) with tetrahalo-1,2-benzoquinones in aprotic media: models for intermediates in catalytic catechol–copper(II) systems*

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Abstract

Tetranuclear copper(I) complexes $[NCuX]_4$ (N = *N,N*-diethylnicotinamide; X = Cl, Br or I) react stoichiometrically with two mol of 3,4,5,6-tetrahalo-1,2-benzoquinones X_4BQ (X = Cl, Br) in aprotic solvents to give tetranuclear products $[NCuX]_4Y_2$. When X = Cl or Br, Y is the corresponding 3,4,5,6-tetrahalocatecholate, which bridges pairs of copper(II) centers in $[NCuX]_4Y_2$. When X = I, Y appears to be the corresponding semiquinone radical in mixed valence products $[NCuI]_4Y_2$. Products $[NCuX]_4Y_2$ differ from those with Y = O or CO_3 in being EPR active in methylene chloride solution at room temperature. Isotropic EPR spectra indicate a very flexible coordination environment for copper(II) and exhibit a sharp signal for a coordinated semiquinone radical when X = I. Lower signal intensity with decreasing temperature suggests that more rigid bridging structures (as exist with Y = O or CO_3 at room temperature) lead to stronger electronic coupling of the copper(II) centers in $[NCuX]_4Y_2$. Products $[NCuX]_4Y_2$ also differ from those with Y = O or CO_3 in being electrochemically active at a platinum electrode in aprotic solvents. The formal potential for $[NCuX]_4Y_2$ reduction decreases sharply on changing X from Cl or Br to I, which also suggests semiquinone-copper(I) character for $[NCuI]_4Y_2$ complexes. Differences between the electronic spectra of $[NCuX]_4Y_2$ with X = Cl or Br and X = I are also consistent with a mixed valence formulation for $[NCuI]_4Y_2$ products.

Introduction

There has been considerable progress in understanding the stoichiometry, products and kinetics of aprotic copper(I)–dioxygen reactions, which are an integral part of all copper-catalyzed dioxygen systems [1–3].

Previous work [3–5] describes tetranuclear halocopper(I) complexes with ligands *N,N*-diethylnicotinamide (N), ethylnicotinate (ENCA) and pyridine (py) and the corresponding tetranuclear oxocopper(II) products of their oxidation with dioxygen in methylene chloride and nitrobenzene. The oxidation products have different ligand-dependent core structures which we have distinguished. Those containing ligand pyridine efficiently initiate and catalyze the oxidative coupling of phenols, whereas those with N and ENCA ligands do not [3, 6].

Kinetic studies indicate insertion of dioxygen into the halo core of $[CuX]_4$ as the rate-determining step of copper(I) oxidation [4, 5]. The rate of oxidation is lower with X = Br than with X = Cl and $[CuI]_4$ cores are not oxidized by dioxygen. Oxidative stability of $[CuI]_4$ cores was explained by especially narrow reactant faces which prevent dioxygen insertion [4]. The tetranuclear oxocopper(II) products $[NCuX]_4O_2$ (X = Cl, Br) are EPR and electrochemically inactive in aprotic solvents at room temperature [4, 5].

Phenols and their oxidation products (quinones) are widespread, important reductants and oxidants, respectively. Oxidation of phenols by oxocopper(II) complexes [3, 7] and reduction of quinones by copper(I) complexes are thus complementary processes.

This paper reports the stoichiometries and products of oxidation of copper(I) complexes $[NCuX]_4$ (X = Cl, Br, I) with formal two-electron oxidants 3,4,5,6-tetrahalo-1,2-benzoquinones, X_4BQ (X = Cl or Br). The products $[NCuX]_4Y_2$ differ from those with Y = O

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or CO_3 in being EPR and electrochemically active. They are considered to be useful models for intermediates in catalytic catechol/copper(II) systems [8–10].

Experimental

Materials

N,N-Diethylnicotinamide (N; Aldrich) was distilled under reduced pressure before use. High purity dinitrogen was deoxygenated by passage through a column of Alfa DE-OX solid catalyst. Copper(I) halides were prepared as described in the literature [11]. Oxidants 3,4,5,6-tetrachloro-1,2-benzoquinone (Cl_4BQ) and 3,4,5,6-tetrabromo-1,2-benzoquinone (Br_4BQ) from Aldrich and the supporting electrolyte tetrabutylammonium perchlorate (Eastman polarographic grade) were used as received.

Synthesis of $[NCuX]_4Y_2$ (X = Cl, Br, I)

A solution of N (2.5 mmol) in anhydrous methylene chloride (25 ml) was flushed with dinitrogen for 15 min. The appropriate copper(I) halide (CuX; 2.5 mmol) was added and the reaction mixture was then stirred with bubbling dinitrogen for 15–20 min. A clear solution was obtained with X = Cl or Br. With X = I, a milky suspension was followed by a white, air-stable precipitate. A dry, deoxygenated solution* of Cl_4BQ or Br_4BQ (1.25 mmol) in methylene chloride (30 ml) was then added with stirring to the preceding solution or mixture. An immediate color change to dark brown was observed as a result of copper(I) oxidation. The brown products $[NCuX]_4Y_2$ were isolated as solids by solvent evaporation and identified by microanalysis and molecular weight determinations (Table 1). Molecular weights, M_r, of all the neutral products were determined by cryoscopy in nitrobenzene (m.p. 5.70 °C, $K_f = 7.00$ °C/molal) [4]. Attempted crystallization of products $[NCuX]_4Y_2$ resulted in disproportionation (see 'Results and discussion').

Physical measurements

Solution electronic spectral measurements were made with Beckman DK-1A and DB-G spectrophotometers in matched quartz cells at room temperature. EPR spectra were recorded at 100 kHz and 6.28 G modulation amplitude with a Bruker Electrospin model EPS 300 spectrometer. Incident power was 100 mW. Resonance conditions were found at *c.* 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. A platinum working electrode (Beckman) and a platinum wire auxiliary electrode were employed in all measurements. All potentials were measured with respect to a saturated calomel electrode, SCE and to the known potential of the ferrocenium/ferrocene couple (0.40 V) [12]. The samples were dissolved in methylene chloride containing 0.1 M tetrabutylammonium perchlorate as the supporting electrolyte. Solutions were deoxygenated with dinitrogen and were kept under an inert atmosphere during electrochemical measurements.

Results and discussion

Copper(I) halides react quantitatively with N in dioxygen-free, weakly coordinating aprotic solvents such as methylene chloride to form tetranuclear complexes $[NCuX]_4$ (X = Cl, Br, I) [4, 5]. The chlorocomplex is the most soluble in all solvents investigated, with $[NCuI]_4$ virtually insoluble. The full, three-dimensional geometry of $[NCuI]_4$ has been determined in an X-ray crystallographic study [4]. The Cu_4I_4 core of the molecule defines a tetrahedrally distorted, cubane-like arrangement with alternating copper(I) and iodide ions. Each d^{10} copper(I) ion is in a tetrahedral coordination environment, being linked to three μ_3-iodide ions and a terminal N ligand. Ligand N is bonded to copper via its ring (pyridyl) nitrogen atom. The six non-bonding Cu---Cu distances average 4.497(36) Å. The corresponding chloro- and bromocopper(I) complexes are very air-sensitive and have not been obtained as single crystals. However, their analytical, spectral and kinetic properties are consistent with the same basic core structure as exists with X = I [4, 5].

Reactions of $[NCuX]_4$ complexes with two mol of 3,4,5,6-tetrahalo-1,2-benzoquinones Cl_4BQ and Br_4BQ

Cryoscopic measurements of the non-electrolyte product solutions from the title reactions were consistent with a stoichiometry given by eqn. (1) (X = Cl, Br, I). All the brown products of eqn. (1)

$$[NCuX]_4 + 2X_4BQ \longrightarrow [NCuX]_4Y_2 \qquad (1)$$

are highly soluble in methylene chloride and nitrobenzene. Cryoscopic and analytical data in Table 1 indicate that $[NCuX]_4Y_2$ are discrete tetranuclear species.

Attempted product crystallization

Many attempts to crystallize products $[NCuX]_4Y_2$ either from saturated solutions or by diffusing an-

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*Cl_4BQ and Br_4BQ can also be added directly as solids, with stirring under dinitrogen, in these syntheses.

TABLE 1. Analytical and cryoscopic data for $[NCuX]_4Y_2$ complexes (X = Cl, Br, I)

Complex	Anal. (%)[a]					M_r[b]
	C	H	N	X	Cu	
$[NCuCl]_4Y_2$[c]	38.8	3.6	6.8	27.2	15.5	1600 ± 30
	(39.0)	(3.5)	(7.0)	(26.6)	(15.9)	(1600)
$[NCuBr]_4Y_2$[c]	35.8	3.4	6.5		13.8	1700 ± 30
	(35.1)	(3.2)	(6.3)		(14.3)	(1780)
$[NCuI]_4Y_2$[c]	32.5	3.1	6.0		12.1	1840 ± 30
	(31.7)	(2.9)	(5.7)		(12.9)	(1970)
$[NCuCl]_4Y_2$[d]	31.9	3.0	5.5		13.3	1900 ± 30
	(31.9)	(2.9)	(5.7)		(13.0)	(1960)

[a] Calculated values in parentheses. [b] Measured in nitrobenzene at the $3\text{–}5 \times 10^{-2}$ molal level [4]. [c] Oxidant in reaction 1 is Cl_4BQ. [d] Oxidant in reaction 1 is Br_4BQ.

hydrous ether into saturated solutions in methylene chloride in a closed system resulted in disproportionation to form brown crystals which analyzed as $N_4Cu_4X_6O$ when X = Cl or Br and unidentified, noncrystalline products when X = I. Disproportionation also occurs on attempted crystallization of $[NCuX]_4Y_2$ (X = Cl or Br; Y = O or CO_3) and other polynuclear oxo(pyridine)copper(II) complexes [5].

Electronic spectra

Electronic spectra data for products $[NCuX]_4Y_2$ of eqn. (1) are listed in Table 2 and illustrated in Figs. 1 and 2. Most of the spectra exhibit intense, broad, split maxima in the region 700–850 nm and absorption minima at 600–650 nm.

Split maxima with large molar absorptivities in the 725–900 nm spectra of polynuclear halo(pyridine)copper(II) complexes indicate five-coordinate copper sites with a minimum of three halo ligands per copper center [4, 6b, 13, 14]. Single broad maxima at *c.* 700 nm with much smaller absorptivity are observed if copper(II) is bonded to fewer than three halo ligands [6b, 14].

The electronic spectra of $[NCuCl]_4O_2$ [4–6] and $[NCuCl]_4Y_2$ are closely similar (Fig. 1). This suggests the same geometrical arrangement around copper in each core structure and that all the copper is present as copper(II). Thus, Cl_4Bz is reduced to coordinated catecholate X_4Cat by $[NCuCl]_4$ in eqn. (1). Since the copper environment in $[NCuCl]_4O_2$ is five-coordinate (three chloro, one pyridyl nitrogen atom and one oxo group) [4, 5], all the copper(II) sites in $[NCuCl]_4Y_2$ are also surrounded by five ligands. Perpendicular catecholate bridges on opposite faces of a cubane structure would satisfy the requirement for five-coordinate copper(II).

It is worth mentioning that the electronic spectrum of $[NCuCl]_4Y_2$ is unaffected by exposure to dioxygen

TABLE 2. EPR and electronic spectral data for $[NCuX]_4Y_2$ complexes (X = Cl, Br, I) in methylene chloride

Complex	EPR			λ_{max} (nm) (ϵ_λ (M^{-1} cm^{-1}))
	298 K		130 K	
	g_i	A_i (G)	g_i	
$[NCuCl]_4Y_2$[a]	2.08	78	2.07	850(810), 785(810)
$[NCuBr]_4Y_2$[a]	2.08	78	2.07	850(1270), 780(1280)
$[NCuI]_4Y_2$[a]	2.08	79	2.08	850(420)[b]
$[NCuCl]_4Y_2$[c]	2.08	79	2.07	850(1400), 775(1340)

[a] Oxidant in reaction (1) is Cl_4BQ. [b] The spectrum of $[NCuI]_4Y_2$ contains no distinct absorption maxima (Fig. 2). Data are given for comparative purposes only. [c] Oxidant in reaction (1) is Br_4BQ.

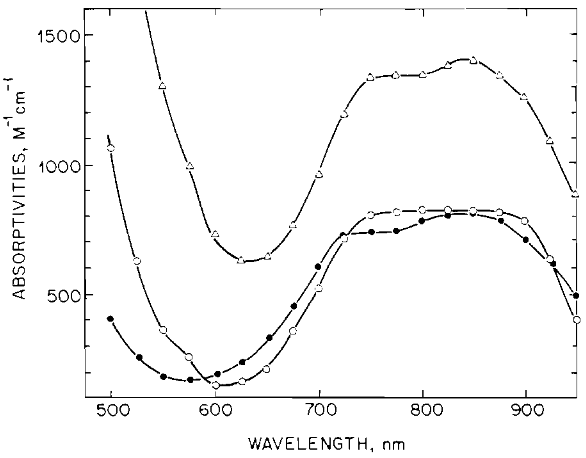

Fig. 1. Electronic spectra of $[NCuCl]_4Y_2$ with $Y = Cl_4Cat$ (○), Br_4Cat (△). Also shown is the spectrum of $[NCuCl]_4O_2$ (●) [5]. The solvent is methylene chloride at 25 °C.

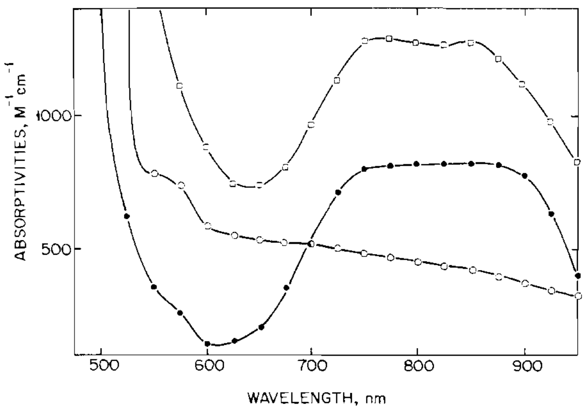

Fig. 2. Electronic spectra of $[NCuX]_4Y_2$, with $X = Cl$ (●), Br (□), I (○) in methylene chloride at 25 °C. Products obtained by use of oxidant Cl_4BQ in reaction (1).

or by the addition of excess Cl_4BQ. This indicates that X_4BQ act as a two-electron oxidant for $[NCuCl]_4$ in eqn. (1) to give oxidatively stable bis-catecholato-copper(II) products [15]*.

When the halo group is altered by changing Cl to Br either in the core itself (as in $[NCuCl]_4Y_2$ ($Y = Cl_4Cat$) to $[NCuBr]_4Y_2$ ($Y = Cl_4Cat$)) (Fig. 2) or in the catecholato bridges (as in $[NCuCl]_4Y_2$ ($Y = Br_4Cat$) (Fig. 1), the absorptivity increases by 56 and 72%, respectively. Similar increases are observed in many polynuclear (halo)pyridinecopper(II) complexes on changing the halide from Cl to Br [4, 5, 16]. This indicates that the near-infrared spectra of $[NCuCl]_4Y_2$ and $[NCuBr]_4Y_2$ in Figs. 1 and 2 are due to copper(II)-centered d–d transitions and not to $Cu \leftrightarrow Y$ charge transfer processes. It also implies complete reduction of Cl_4BQ and Br_4BQ to the corresponding catecholates by copper(I).

By contrast, tetranuclear products $[NCuI]_4Y_2$ exhibit very unusual featureless spectra that have much lower absorptivities than for the chloro and bromo analogues (Fig. 2). The lack of characteristic absorption maxima for copper(II) and the low absorptivities suggest incomplete $[NCuI]_4$ oxidation by Cl_4BQ and Br_4BQ. It appears that the four copper(I) centers of $[NCuI]_4$ are not all oxidized to copper(II) by these oxidants, and that Y in the products is best represented as the semiquinone radical anion. This would mean that $[NCuI]_4Y_2$ are mixed valence products (see below).

EPR spectra

X-band EPR spectra of $[NCuX]_4Y_2$ ($X = Cl$, Br, I) (1.0 mM) were measured in methylene chloride at 298 and 130 K. The data are collected in Table 2 and illustrated in Figs. 3 and 4.

The room temperature spectra (Fig. 3) are isotropic (average $g_i = 2.08$ and $A_i \simeq 79$ G) in all cases. A dramatic decrease in intensity to give very broad, isotropic resonances ($g \simeq 2.07$) was observed at 130 K (Fig. 4). Close similarity of these EPR spectra suggests a similar geometrical environment for each EPR active copper(II) site regardless of variations in electron density with varying X in the core or in the Y bridges [17]. Of particular note is the very

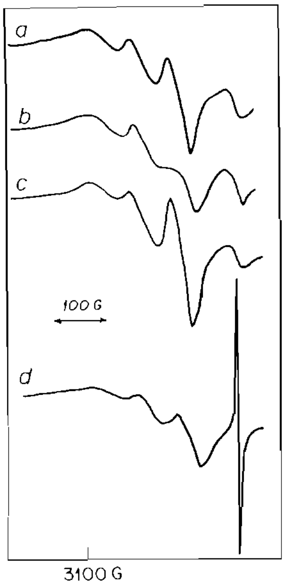

Fig. 3. EPR spectra of $[NCuX]_4Y_2$ (1.0 mM) in methylene chloride at 25 °C with (a) $X = Cl$, oxidant Br_4BQ in reaction (1); (b) $X = Cl$, oxidant Cl_4BQ; (c) $X = Br$, oxidant Cl_4BQ; (d) $X = I$, oxidant Cl_4BQ. Sensitivity is 3.2×10^5.

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*IR spectroscopy is not very useful for distinction between coordinated X_4BQ and coordinated X_4Cat in the products of eqn. (1) because of overlapping bands from ligand N. However the stoichiometric and electronic spectral data strongly suggest reduction of X_4BQ to X_4Cat and complete oxidation of copper(I) to copper(II) in these reactions.

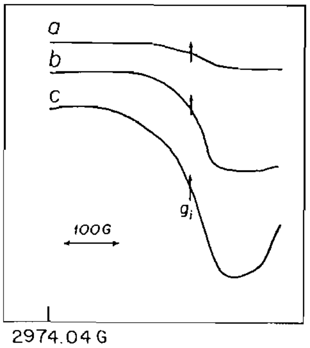

Fig. 4. EPR spectra of $[NCuX]_4Y_2$ (1.0 mM) in methylene chloride at 130 K: (a) X=Cl; (b) X=Br; (c) X=I. The oxidant was Cl_4BQ in reaction (1). Sensitivity is 8.0×10^4.

sharp resonance at $g=2$ for $[NCuI]_4Y_2$ in Fig. 3(d). This is taken as a further indication that $[NCuI]_4Y_2$ contain semiquinone forms of Y, each of which has an unpaired electron.

The molecules $[NCuX]_4O_2$ are EPR silent in methylene chloride at room temperature and 77 K [5]. This indicates strongly coupled copper(II) centers as a result of the presence of μ-oxo units. Replacement of oxo with catecholate or semiquinone bridges evidently decreases this coupling to give low-intensity isotropic EPR spectra at low temperatures.

Redox chemistry

The redox behavior of Cl_4BQ, Y^{2-} (obtained by adding a five-fold excess of pyridine to 3,4,5,6-tetrachlorocatechol, YH_2) and $[NCuX]_4Y_2$ (X=Cl, Br, I; Y derived from Cl_4BQ in eqn. (1)) was examined by cyclic voltammetry at the 1.0 mM level in methylene chloride containing 0.1 M tetrabutylammonium perchlorate as the supporting electrolyte. All the solutions were flushed with deoxygenated dinitrogen for at least 5 min before each measurement at room temperature. Typical data are illustrated in Fig. 5.

Quasi-reversible electrochemistry with single peaks for reduction and oxidation was observed for all species except $[NCuI]_4Y_2$. The formal reduction potentials E_f for samples Cl_4BQ, Y^{2-} and $[NCuX]Y_2$ (X=Cl and Br) were 0.17, 0.42, 0.80 and 0.80 V versus SCE, respectively, with a maximum uncertainty of ±0.02 V in each estimate. Thus, electrochemistry of $[NCuX]Y_2$ complexes seems to be associated with their coordinated catecholato ligands.

By contrast, $[NCuI]_4Y_2$, where Y is derived from reaction (1) with oxidant Cl_4Bz, is irreversibly reduced at -0.04 V versus SCE. The much more negative potential for reduction and the lack of oxidative activity with X=I suggest that iodide preferentially stabilizes copper(I) [18, 19]. As a result, the entities Y in $[NCuI]_4Y_2$ appear to be semiquinones and not

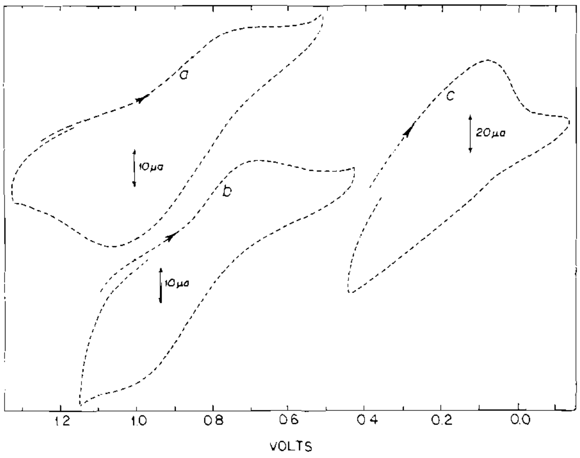

Fig. 5. Cyclic voltammograms of complexes $[NCuX]_4Y_2$ (1.0 mM) with (a) X=Cl; (b) X=Br; (c) X=I, in methylene chloride containing tetrabutylammonium perchlorate (0.1 M) at a platinum electrode vs. SCE under dinitrogen. The oxidant in reaction (1) was Cl_4BQ. The scan rate is 200 mV s^{-1} and the temperature is 25 °C.

catecholates. This formulation would be consistent with their EPR and spectral properties (see above).

Conclusions

Although $[NCuI]_4$ is stable in the presence of dioxygen, it is easily oxidized by X_4BQ, which are formal two-electron oxidizing agents (eqn. (1)). All the products $[NCuX]_4Y_2$ are EPR and electrochemically active in methylene chloride at room temperature, which is not the case for $[NCuX]_4O_2$ or $[NCuX]_4(CO_3)_2$ complexes. Electrochemical activity of $[NCuX]Y_2$ seems to be associated with their catecholate or semiquinone ligands Y created by copper(I) reduction of X_4BQ in reaction (1). Complete reduction of X_4BQ to the corresponding catecholate seems only to occur with X=Cl or Br in reactants $[NCuX]_4$.

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