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Unusually stable peroxocopper complexes. Stoichiometry, products and kinetics of oxidation of the dimeric copper(I) complex $[LCuBr]_2$ (L = *N,N'*-diethylethylenediamine) by dioxygen in methylene chloride from −51 to 30 °C

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Abstract

Copper(I) bromide dissolves in deoxygenated methylene chloride and nitrobenzene solutions of equimolar *N,N'*-diethylethylenediamine (DEED) to give the colorless copper(I) dimer $[(DEED)CuBr]_2$ (**D**). Dioxygen uptake, analytical, cryoscopic, spectral and kinetic data show that **D** is oxidized to the blue tetranuclear mixed valence peroxocomplex $[(DEED)CuBr]_4O_2$ (**A**) at temperatures from −51 to 30 °C. The rate law is $d[A]/dt = k_{DL}[O_2][D]^2$ with activation parameters $\Delta H^{\ddagger}_{DL} = -1.8 \pm 0.4$ kcal mol^{-1} and $\Delta S^{\ddagger}_{DL} = -38 \pm 5$ cal deg^{-1} mol^{-1} at 25 °C. These parameters resemble those for third-order oxidation of the copper(I) dimer $[(TEED)CuCl]_2$ (TEED is *N,N,N',N'*-tetraethylethylenediamine) to the peroxocopper product $[(TEED)CuCl]_4O_2$ at low temperatures. They are completely different from those for direct, third-order oxidation of $[LCuX]_2$ dimers to the oxocopper(II) products $[LCuX]_2O$ at ambient temperatures because of slow transfer of the third electron from copper(I) to O_2 in ambient $[(DEED)CuBr]_2/O_2$ and low temperature $[(TEED)CuCl]_2/O_2$ reactions. As observed in the $[(TEED)CuCl]_2/O_2$ system, primary product **A** relaxes to a different tetranuclear copper complex **B**, with **A** thermodynamically favored at higher temperatures up to −17 °C. First-order decomposition of **A** to give 2 mol of the oxocopper(II) product $[(DEED)CuBr]_2O$ (**C**) has an exceptionally long half-life of 3.2 ± 0.1 h at 25 °C. The resistance of **A** to intramolecular copper(I) → peroxide electron transfer with L = DEED and X = Br is attributed to (i) hydrogen bonding between the N–H groups of DEED and bound peroxide and (ii) stabilization of copper(I) by Br.

Key words: Kinetics and mechanism; Copper complexes; Peroxo complexes; Bidentate ligand complexes; Chelate complexes

Introduction

Copper(I) prefers two- and four-coordination in the solid state [1] but its d^{10} configuration and relatively low effective nuclear charge lead to wide, ligand-dependent variations in its solution properties, reactivity and reaction mechanisms.

Cu_{aq}^{+} destroys itself unless deliberately destroyed, eqns. (1) and (2) [2]. It is so stabilized by π-acid acetonitrile (AN) that copper(II) in solvent AN is

$$2Cu_{aq}^{+} \longrightarrow Cu_{aq}^{2+} + Cu^0 \qquad (1)$$

$$Cu_{aq}^{+} + (NH_3)_5CoF_{aq}^{2+} + 5H_{aq}^{+} \longrightarrow Cu_{aq}^{2+} + 5NH_4^{+} + Co_{aq}^{2+} + F_{aq}^{-} \qquad (2)$$

strongly oxidizing [3]. Air-stability of labile $[(AN)_4Cu]A$ complexes ($A = BF_4^-$, PF_6^-, etc.) makes them convenient sources of aminecopper(I) complexes [4–11] but the kinetics of aqueous copper(I)–O_2 reactions in the presence of monodentate amines [4] and AN [5] are complicated by competing equilibria. In aprotic solvents, copper(I) oxidizability with O_2 strongly depends on the ligand and molar ligand/copper(I) ratio [6–8].

Copper(I)/O_2 reactions play key roles in many copper-catalyzed processes. Work by Karlin and co-workers

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[7] and Kitajima *et al.* [8] simulates biochemical copper(I)–dioxygen reactions. Careful choice of polydentate ligands P limits the number of electrons transferred to O_2 and gives the soluble products $[PCu]_2O_2^{2+}$ with different arrangements of bridging peroxide that can be distinguished structurally [7, 8], kinetically [9] and chemically [10, 11]. These peroxocopper complexes survive in aprotic solvents near −80 °C but rapidly decompose at higher temperatures. Factors that limit the number of electrons transferred to O_2 and stabilize peroxocopper complexes need to be established so that copper-catalyzed oxidation mechanisms can be understood [7–9, 12].

Copper(I) halides are also convenient sources of copper(I). Their monodentate amine complexes may be monomers, dimers, tetramers or polymers in the solid state [1] but the nuclearity (monomer, dimer or tetramer) in aprotic solvents can be controlled by choice of experimental conditions [13]. Copper(I) halides have a high affinity for polyamines. The diamine complexes are halo-bridged LCu(X, X)CuL dimers with Cu...Cu distances from 2.56 to 2.73 Å [14].

Most halo(amine)copper(I) complexes are air-sensitive*. Our work addresses the mechanisms of important industrial reactions [17] that are homogeneously catalyzed by their reactions with O_2 in aprotic solvents, eqns. (3) and (4) [12, 13, 15, 16, 18–20], where the ligands are *N,N,N′,N′*-tetraalkyldiamines (L) [12, 20–23] or monodentate pyridines (N) [13, 15, 18, 19] and X is Cl or Br. The state of oxygen in the

$$2[LCuX]_2 + O_2 \longrightarrow 2[LCuX]_2O \qquad (3)$$

$$[NCuX]_4 + O_2 \longrightarrow [NCuX]_4O_2 \qquad (4)$$

products is of very special interest. Reactions (3) give neutral, green μ-oxo dimers with absorption maxima near 700 nm [21–23], while the products with ligands N (eqn. (4)) are neutral, brown oxo(halo)–pyridinecopper(II) tetramers with characteristic split absorption maxima in the 750–850 nm region [13, 18, 19]. The oxo group dispositions in $[NCuX]_4O_2$ depend on N [13, 15, 18, 19]. This disposition determines their proton basicity, which is an important factor in copper-catalyzed oxidations of protic substrates such as phenols [4–13, 16–24].

The nuclearities of $[LCuX]_2$ and $[NCuX]_4$ determine their ambient oxidation rate laws because of the strong thermodynamic tendency for total O_2 reduction to give oxocopper(II) products [13, 15, 18–23]. Oxidations of dimers $[LCuX]_2$ (X = Cl, Br) characteristically are third-order, eqn. (5) [22], while tetramers $[NCuX]_4$ are oxidized with second-order rate law (6) [13, 18, 19]. The slowest step in (3) is assembly of the activated complex

$$d[[LCuX]_2O]/dt = k_D[O_2][[LCuX]_2]^2 \qquad (5)$$

$$d[[NCuX]_4O_2]/dt = k_T[O_2][[NCuX]_4] \qquad (6)$$

from two $[LCuX]_2$ dimers and one O_2 [22, 23], while reactions (4) depend on slow penetration of the X_4 cores of $[NCuX]_4$ by O_2 [13, 18, 19].

The transfer of four electrons from copper(I) to oxygen is so fast at ambient temperatures that no intermediate oxidation states have been detected in either case. However, work with dimeric copper(I) reductant $[(TEED)CuCl]_2$ (**D**: L = TEED is *N,N,N′,N′*-tetraethylethylenediamine) demonstrates that neutral $[LCuX]_2/O_2$ reactions proceed via identifiable peroxo complexes at low temperatures [23]. Scheme 1 summarizes the results. Oxidation of **D** is third-order at ambient (eqn. (5), X = Cl) or lower temperatures (eqn. (7)) but third-order rate constants k_D and k_{DL} have

$$d[A]/dt = k_{DL}[O_2][[LCuX]_2]^2 \qquad (7)$$

very different activation parameters because they refer to different rate-determining steps. There is no evidence for significant concentrations of species **A′** in Scheme 1 from one-electron transfer at −80 °C. The primary peroxocopper product $[(TEED)CuCl]_4O_2$ (**A**) has higher nuclearity than $[PCu]_2O_2^{2+}$ complexes [8–11] evidently because of the need to transfer two electrons to O_2 from separate dimers **D** with short Cu...Cu separations [14].

Peroxocomplexes **A** and **B** (Scheme 1) exist in slow equilibrium in the temperature range −78 to −50 °C. Conversion of **A** to **B** is exothermic and species **A** predominates at higher temperatures. However, **A** is irreversibly converted to the oxocopper(II) dimer $[(TEED)CuCl]_2O$ (**C**) with a half-life of 25 s at −35 °C in reaction (8) [23].

$$\mathbf{A} \longrightarrow 2\mathbf{C} \qquad (8)$$

We see that the product $[(TEED)CuCl]_4O_2$ survives at low temperatures because of kinetic requirements for intramolecular transfer of the third electron to break the O–O bond in **A** and **B**. The most important conclusion [23] is that chloride and the hard, fully alkylated diamine ligand TEED do not stabilize neutral peroxocopper complexes **A** and **B** at ambient temperatures.

The present work explores factors that increase this stability. We report that changing the halide from chloride to bromide and the amine ligand L from TEED to *N,N′*-diethylethylenediamine (DEED) gives analogous peroxocopper complexes **A** and **B** (Scheme 1) but with a half-life for reaction (8) of 3.2 ± 0.1 h at 21 °C in methylene chloride. The special stability of **A** is attributed to (i) hydrogen-bonding between the N–H

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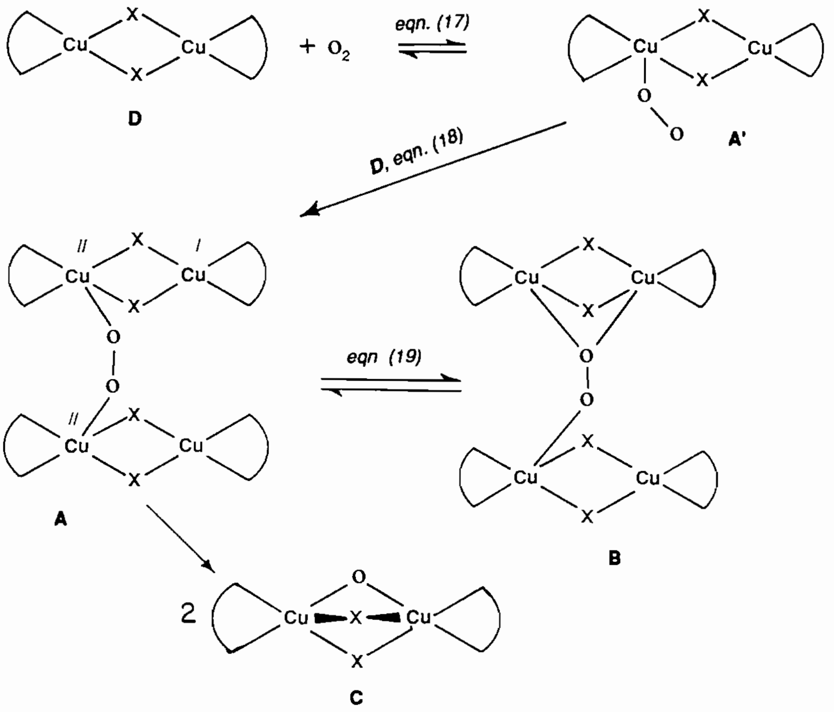
*Exceptions include $[NCuI]_4$ (N = py and *N,N*-diethylnicotinamide) [15] and complexes of copper(I) halides with *N,N,N′,N′*-tetrabenzylethylenediamine and 2-(2-(dimethylamino)ethyl)-pyridine [1, 16].



Scheme 1.

groups of DEED and bound peroxide and (ii) stabilization of copper(I) in **A** and **B** by Br.

Experimental

Materials

Copper(I) bromide was made from $CuBr_2$ by the literature method [25]. *N,N'*-Diethylethylenediamine (DEED, Aldrich) was vacuum distilled immediately before use. $^{18}O_2$ (98% isotopic purity) was purchased from Icon Services, Inc. and used as received. All other reagents and solvents were reagent grade or were purified in our laboratories by established methods [13]. Elemental analyses were performed by Desert Analytics, Tucson, AZ.

Synthesis of $[(DEED)CuBr]_2$ (D), $[(DEED)CuBr]_4O_2$ (A), $[(DEED)CuBr]_2O$ (C) and $[(DEED)CuBr]_2CO_3$ (E)

In a typical experiment, DEED (10 mmol) was dissolved in anhydrous methylene chloride (100 ml) under N_2 at −80 °C. CuBr (10 mmol) was then added and the mixture was stirred under N_2 until a colorless solution was obtained. Attempted isolation of product $[(DEED)CuBr]_2$ (**D**) gave a colorless solid that was too air-sensitive to give reproducible analytical data. However, cryoscopic measurements on product solutions in nitrobenzene at 5 °C [13a] indicated the formation of dimer $[(DEED)CuBr]_2$ (**D**) (see Table 1).

Treatment of **D** in methylene chloride at −50 or 25 °C with excess O_2 resulted in rapid formation of a blue solution whose electronic spectrum varied little with temperature (small variations are due to $\mathbf{A} \rightleftarrows \mathbf{B}$ equilibration, eqn. (19), see below). Vacuum evaporation of the methylene chloride solvent gave the blue–green solid $[(DEED)CuBr]_4O_2$ (**A**, Table 1). Attempted crystallization of **A** with a variety of room and low-temperature techniques was unsuccessful because of its slow decomposition to **C**, eqn. (8). Dioxygen uptake measurements on solutions of **D** in nitrobenzene at 25 °C with a standard Warburg apparatus indicated the stoichiometry of eqn. (9).

$$2\mathbf{D} + O_2 \longrightarrow [(DEED)CuBr]_4O_2\ (\mathbf{A}) \qquad (9)$$

The oxocopper(II) dimer $[(DEED)CuBr]_2O$ (**C**) was obtained by allowing solutions of **A** in methylene chloride to stand for 24 h at room temperature, eqn. (8). Manometric measurements on solutions of **C** in nitrobenzene at 25 °C confirmed that coordinated DEED is not oxidized at a significant rate in reactions (8) or (9). Evaporation of the solvent from reaction (8) in methylene chloride gave pure samples of solid complex **C** (Table 1).

The carbonatocopper(II) dimer $[(DEED)CuBr]_2CO_3$ (**E**) was obtained (i) by allowing a carbon dioxide-saturated solution of **A** in methylene chloride to decompose at room temperature, eqn. (10), or (ii) by treating a solution of fully formed **C** in methylene chloride with excess CO_2 at 25 °C, eqn. (11). Vacuum evaporation of the solvent gave pure solid samples of **E** from either procedure.

$$\mathbf{A} + 2CO_2 \longrightarrow 2[(DEED)CuBr]_2CO_3\ (\mathbf{E}) \qquad (10)$$

$$\mathbf{C} + CO_2 \longrightarrow \mathbf{E} \qquad (11)$$

Analytical, cryoscopic, molecular weight and spectral data for **D**, **A**, **C** and **E** are given in Table 1.

Chemical identification of peroxide in A

Two test solutions were used for the qualitative identification of peroxide in product **A**. The first (**F**, 100 ml) consisted of a saturated solution of KI in methylene chloride containing 10 mmol of $HBF_4 \cdot Et_2O$. The second (**G**) consisted of 100 mg t-butylammonium iodide and 10 mmol $HBF_4 \cdot Et_2O$ in 100 ml methylene chloride. Tests were conducted with as-prepared or deoxygenated **F** or **G** at room temperature.

Additions of freshly made solutions of **A**, freshly isolated solid **A**, H_2O_2 or I_2 to **F** or **G** gave the distinct pink color of I_2, but additions of solid or solution samples of **C** or **E** gave a brown color. Randomly chosen colleagues were easily able to distinguish **C** and **E** from blind samples containing peroxide.

The peroxide content of **A** was determined as follows. A solution of 0.3125 mmol of freshly prepared **A** in methylene chloride (10 ml) was treated with 2 ml of $HBF_4 \cdot Et_2O$ and excess peroxide-free diethyl ether. The precipitated solid was removed by centrifugation, the ether layer was shaken with 5.0 g anhydrous KI and the mixture was centrifuged. Titration of the separated supernatant to a colorless endpoint required 22.0 ml of 0.030 M aqueous $Na_2S_2O_3$. A control experiment with 0.3125 mmol of oxocopper(II) complex $[NCuCl]_4O_2$ (N = *N*,*N*-diethylnicotinamide [13a]) instead of **A** required 4.5 ml of the $Na_2S_2O_3$ solution to discharge the yellow color. The peroxide content of the sample of **A** is thus 0.26 mmol, which is 83% of the expected value. The discrepancy is due to partial decomposition of **A** during sample workup.

These experiments identify **A** as a peroxocopper complex through reaction (12).

$$[(DEED)CuBr]_4O_2 + 2I^- + 4H^+ \longrightarrow 2H_2O + I_2 + \text{other products} \qquad (12)$$

Physical measurements

The molecular weights of **D**, **A**, **C** and **E** were determined by cryoscopy in nitrobenzene (f.p. 5.00 °C; $K_f = 7.00$ °C/m) [13a]. Electronic spectra of reactants and products 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. IR spectra of solid products (KBr disk) and their solutions in methylene chloride (NaCl plates) were obtained with Perkin-Elmer model 567 and Mattson FTIR model 4200 Galaxy Series spectrometers. EPR spectra of solid products and their 1.0 mM solutions 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 *c*. 9.39 GHz (X-band) at room temperature and 130 K. A number of instruments and experimental conditions were employed in attempts at Raman spectroscopic identification of peroxide in **A** (*vide infra*).

Kinetic measurements

The reaction of $[(DEED)CuBr]_2$ (**D**) with O_2 in methylene chloride proceeds in three distinct and easily resolvable steps. The kinetics of the first step (eqn. (9)) and the second step (eqn. (19)) were monitored

TABLE 1. Analytical, cryoscopic molecular weight and electronic spectral data for complexes **D**, **A**, **C** and **E**

Label	Complex	Anal.[a,b] (%)					M_r[c]	λ_{max} (nm) (ϵ_{max}(M^{-1} cm^{-1}))[d]
		C	H	N	Cu	Br		
D	$[(DEED)CuBr]_2$						515 ± 30 (535)	–[e]
A	$[(DEED)CuBr]_4O_2$	26.5 (26.9)	5.8 (6.0)	9.9 (10 5)	23.6 (23.1)	29.5 (29.0)	1190 ± 30 (1102)	650(170)[f] 380(sh, 390)
C	$[(DEED)CuBr]_2O$	26.4 (26.9)	5.9 (6.0)	9.9 (10.5)	23.0 (23.1)	29.5 (29.0)	560 ± 20 (551)	660(210) 380(sh, 480)
E	$[(DEED)CuBr]_2CO_3$	26.4 (26.9)	5.6 (5.5)	9.1 (9.7)	23.9 (23.1)	27.0 (27.6)	580 ± 20 (595)	650(140)

[a] Calculated values in parentheses. [b] Solid complex **D** is too air-sensitive to give reproducible elemental analytical data. [c] Measured in nitrobenzene at the $3–5 \times 10^{-2}$ molal level [13a]. [d] In methylene chloride at 25 °C. [e] No spectral features in the region 350–900 nm. [f] Since **A** is postulated to contain two formal copper(II) centers (Scheme 1) and **D** has negligible absorption in this region, the absorptivity per copper(II) center in **A** is 85 (g atom Cu^{II})$^{-1}$ cm^{-1}.

at 600 nm in the temperature range −51.0 to 30.0 °C in a DEC PRO380 computer-assisted Hi-Tech SFL41 stopped-flow spectrophotometer. The concentration ranges employed were [**D**] = 2.91–17.5 mM, with $[O_2]_0 = 0.22$–0.44 mM. Reactant **D** was always present in sufficient excess to favor total O_2 reduction under pseudo-first-order conditions. Respective observed pseudo-first-order rate constants $k_{obs}(1)$ and $k_{obs}(2)$ were obtained from the slopes of plots of $\ln|A_\infty - A_t|$ versus time, where A_t is the absorbance at time t.

Rate constants $k_{obs}(3)$ for the last reaction step (eqn. (8)) were obtained by conventional spectrophotometry at 450 nm in the temperature range 10.0–26.0 °C with $[A]_0 = 0.88$–1.84 mM in the absence and presence of O_2.

Each run was repeated at least three times under fixed experimental conditions. The maximum error in a given rate constant is ±5%.

Results and discussion

General observations

Dioxygen is a four-electron oxidant; each halo(amine)copper(I) center is a one-electron reductant [1, 13, 18–20, 22, 23]. However, monomers py_2CuX [13] and py_3CuCl [26] (py = pyridine) are not oxidized to detectable superoxocopper(II) complexes in aprotic solvents because the latter are very rapidly reduced by excess copper(I) at ambient temperatures, eqn. (13) [13a]. The reactions are exothermic with large driving forces because of the formation of strong oxocopper(II) bonds in the ultimate products $[pyCuX]_4O_2$. Rate law (14) for reactions (13) was the first clue that the crucial step is transfer of the third electron from copper(I) to O_2 to break its O–O bond [13a]. We can now understand rate laws (5) and (6) for reactions (3) and (4), respectively: more than three electrons are available in the activated complex for reaction (3), the reactant in eqn. (4) is a four-electron reductant and there are no significant kinetic barriers to total O_2 reduction by copper(I) at ambient temperatures.

$$4py_mCuX + O_2 \longrightarrow [pyCuX]_4O_2 + 4(m-1)py \qquad (13)$$

$$d[[pyCuX]_4O_2]/dt = k_M[O_2][py_mCuX]^3 \qquad (14)$$

The thermal stability of peroxocopper complexes depends on several factors [12]. If the copper(I) center is a cation with several monodentate amine ligands [6, 7] or carries a bulky polydentate amine ligand P [6–10], then the primary peroxoproduct of eqn. (15) can result from a large equilibrium constant and a stoichiometry $\Delta[\text{product}]/\Delta[O_2] = 1.0$. However, reversibility of reactions (15) has been demonstrated in several systems [9–11]. As in any other metal–ligand interaction, the positive charge of $[PCu]_2O_2^{2+}$ helps to bind peroxide. This leaves little excess reductant for reaction (16), which in any event is slower than (15) at low temperature. The alternative is when reaction (15) is not strongly favored but reaction (16) is still slow because the reactants are bulky cations [7–12].

$$2PCu^+ + O_2 \rightleftharpoons [PCu]_2O_2^{2+}\,\text{fast} \qquad (15)$$

$$[PCu]_2O_2^{2+} + 2PCu^+ \longrightarrow \text{oxocopper products} \qquad (16)$$

Neutral halo(diamine)copper(I) dimers $[LCuX]_2$ with weak π-acceptor ligands L and X resort to other means of stabilizing coordinated peroxide because of their short Cu...Cu separations [14]. Two $[LCuX]_2$ dimers are used for this purpose (Scheme 1) [23]. The resulting assemblies **A** or **B** have the four electrons needed to completely reduce O_2 to oxide but they sometimes survive at low temperatures because of a kinetic barrier for transfer of the third electron to O_2 [12]. This barrier (estimated at 25 kcal mol^{-1} when L is TEED and X is Cl in **D**) [23] separates **A** from ultimate oxocopper(II) dimer **C**, which contains stronger copper–oxygen bonds than **A** or **B** (Scheme 1). Greater Cu–O bond strength provides the driving force for the overall reaction.

Given that peroxo complexes **A** and **B** (L = TEED, X = Cl) are stable enough to be characterized at temperatures below *c.* −40 °C, we asked ourselves what ligand modifications might increase their stability. We knew that bromide and iodide are better stabilizers of copper(I) than chloride [20, 27]*. We also knew that coordinated peroxide and oxide are basic and may be stabilized by hydrogen bonding with the ligand [28]. We hesitated to use DEED as the ligand because replacement of some of the N–ethyl groups in TEED with N–H might lead to ligand oxidation [16, 22, 29]. These fears were dispelled by establishment of the stoichiometry of reaction (9) by dioxygen uptake measurements and by the observation that CO_2 does not insert into the N–H groups of coordinated DEED in reactions (10) and (11).

Products of oxidation of $[(DEED)CuBr]_2$ by dioxygen

The data in Table 1 indicate that, like other neutral halo(*N*-alkyldiamine)copper(I) complexes [12, 14, 20–23, 29], the title reductant exists as discrete dimers in aprotic solution. Copper(I) chloride forms cubane tetramers $[py_2CuCl]_4$ and $[(ENCA)_2CuCl]_4$ (ENCA is ethylnicotinate) that contain five-coordinate copper(I). These tetramers readily dissociate to dimers $[py_2CuCl]_2$ and $[(ENCA)_2CuCl]_2$ containing four-coordinate copper(I) at low or moderate total CuCl concentrations [13a]. Tetramers $[LCuX]_4$ (L = diamine, X = Cl, Br or

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*Unfortunately, dimer $[(DEED)CuI]_2$ is not sufficiently soluble in methylene chloride to allow a detailed study of the kinetics of its reactions with O_2.

I) with a cubane [15] core structure would contain five-coordinate copper(I), which is rare even in the solid state [1]. We know of no evidence for the existence of $[LCuX]_4$ tetramers. Dimers $[LCuX]_2$ dissociate to monomers LCuX in coordinating solvents like AN[14].

The stoichiometry of oxidation of $[(DEED)CuBr]_2$ by dioxygen to give **A** is $\Delta[[(DEED)CuBr]_2]/\Delta[O_2] = 2.0 \pm 0.1$, eqn. (9). However, because of the low rate of reaction (8) we can isolate peroxo product **A** (Scheme 1) as a solid. The data in Table 1 indicate that **A** is a tetranuclear complex with the same elemental analysis as its ultimate decomposition product $[(DEED)CuBr]_2O$ (**C**) from eqn. (8). The data also indicate that **A** and **C** react with excess CO_2 to give the dimeric carbonato derivative $[(DEED)CuBr]_2CO_3$ (**E**) in reactions (10) and (11).

Electronic spectra of D, A, C and E

Copper(I) complex **D** has very low absorptivity and no spectral features in the 350–900 nm region. Its oxidation products **A**, **C** and **E** have broad d–d bands at 650–660 nm and absorption minima at 480–520 nm (Fig. 1). These d–d spectra resemble those of other well-characterized dimeric $[LCuX]_2Y$ complexes ($Y = O$ or CO_3) [12, 20–23] and indicate that the copper(II) centers of the oxidation products carry less than three bromo ligands [30]. This eliminates the possibility that **A** are oxocopper(II) tetramers produced directly in reactions (4) [30]. The molar absorptivities of **A**, **C** and **E** are larger with DEED, Br ligands than with TEED, Cl ligands [21, 23].

The spectra of **A** and **C** exhibit broad shoulders near 380 nm. Spectral shoulders at about the same wavelength for **A** (L = TEED, X = Cl) [23], **A** (L = DEED, X = Br) and oxocomplex $[(TEED)CuBr]_2O$ (**C**) might be taken to indicate that **A** are tetranuclear oxocopper(II) complexes $[LCuX]_4O_2$ like those formed in reactions (4) with monodentate pyridine ligands [13–15]. However, (i) the latter have characteristic d–d electronic spectra with broad overlapping bands at 775 and 850 nm due to coordination of three halide ligands per copper(II) center [30] and differ markedly from those in Fig. 1; (ii) copper(II) coordination number five is commonly observed in tetranuclear oxo(pyridine)copper(II) complexes; (iii) we know of no evidence for six-coordinate copper(II) centers in tetranuclear structures with only amine, halo and oxo ligands on copper; (iv) complexes **A** (L = TEED, X = Cl [23] and L = DEED, X = Br (this work)) contain peroxo ligands; (v) the characteristics of relaxation reaction (19) are not consistent with conversion of oxo complexes $[LCuX]_4O_2$ to tetranuclear oxo species containing copper(II) centers with lower coordination numbers, which would be irreversible [13a]; and (vi) we know of no evidence for the existence of tetranuclear complexes $[LCuX]_4Y_2$ (L = diamine, X = Cl, Br, I; Y = O, CO_3).

Infrared spectra

IR spectra of DEED and products **D**, **A**, **C** and **E** were obtained for the solids and their solutions in methylene chloride. Differences were found in the 1300–1700 cm^{-1} region, which is characteristic of N–H bending in the DEED ligand [31]. Figure 2 shows that

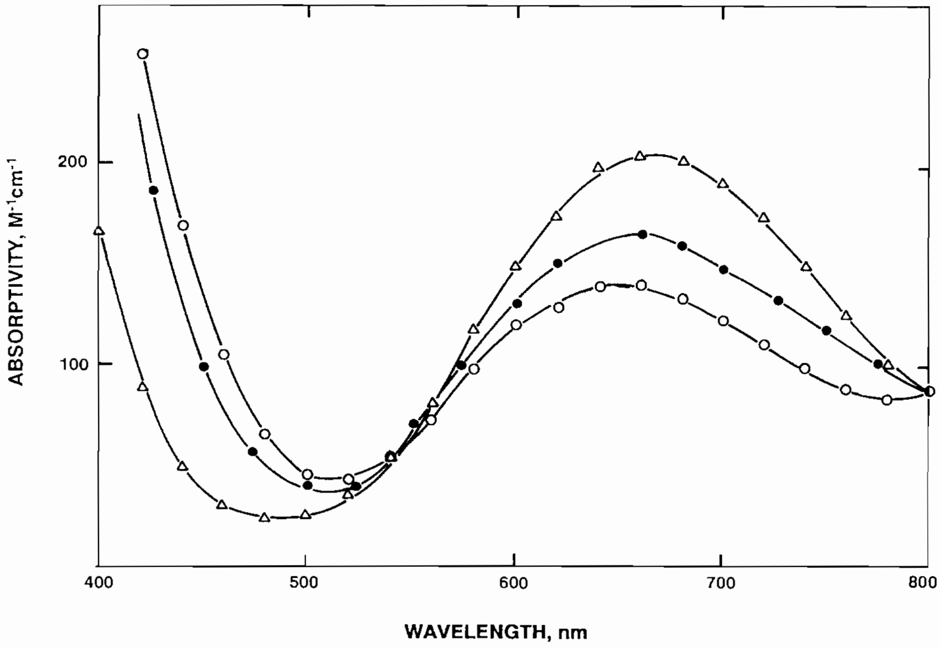

Fig. 1. Electronic spectra of **A** (●), **C** (△) and **E** (○) in methylene chloride at 25 °C.

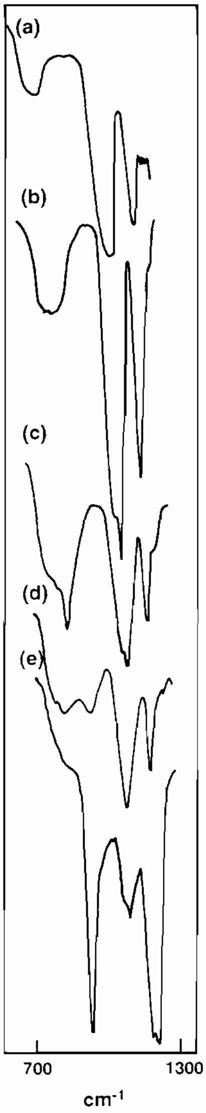

Fig. 2. IR spectra of neat (a) DEED; (b) **D**, (c) **C**; (d) **A**; (e) **E**.

coordination of DEED to copper(I) in **D** has little effect on its IR spectrum in this region. However, coordination of DEED in **A** causes distinct changes that are also apparent for **C** and **E**. The broad peak for **D** becomes a resolved doublet at 1615, 1540 cm^{-1} in **A** but sharp singlets at 1600 and 1550 cm^{-1}, respectively, are observed in **C** and **E**. The simplest explanation for these differences is that the N–H groups of DEED are involved in hydrogen bonding with the peroxo group of **A** and with the oxo and carbonato groups of **C** and **E**, respectively.

EPR spectra

The EPR spectra of oxidation products **A**, **C** and **E** are summarized in Table 2. EPR activity indicates that **A**, **C** and **E** are paramagnetic, as observed in the $[(TEED)CuCl]_2/O_2$ system [23]. The EPR spectra are axial, which is characteristic of copper(II) complexes with a $d_{x^2-y^2}$ ground state and square-pyramidal geometry about copper [32]. The paramagnetism of the carbonato product **E** indicates that it has an asymmetrical carbonato bridge between the copper(II) centers, a *cis* arrangement of its bromo ligands or both of these structural features [20–22].

TABLE 2. EPR spectral data for complexes **A**, **C** and **E**

Complex	State	Temp.[a]	$A_{\parallel}$[b]	$g_{\parallel}$	$g_{\perp}$	$\langle g \rangle$
A	c	130	180	2.27	2.03	2.11
	c	300	160	2.26	2.04	2.11
C	c	130	150	2.27	2.05	2.12
	c	300	180	2.28	2.05	2.12
	d	130		2.27	2.03	2.11
	d	300				2.15
E	c	130	200	2.24	2.00	2.08
	c	300	170	2.28	2.02	2.10
	d	130	160	2.28	2.03	2.11
	d	300				2.15

[a]Temperature in degrees K. [b]Units are 10^{-4} cm^{-1}. [c]Solid sample. [d]In methylene chloride solution.

Detection of peroxide

Product **A** (Scheme 1, L = TEED, X = Cl) has features in its Raman spectrum at 822 and 842 cm^{-1} that are absent in the spectrum of its decomposition product $[(TEED)CuCl]_2O$ [23]. Despite careful work involving solid and solution product samples in six different Raman spectrometers with excitation wavelengths in the range 4579–5145 Å and temperatures between −80 and 25 °C, we could detect no ν(O–O) stretching bands for peroxide in **A** or **B** (L = DEED, X = Br)*. Our explanation for these results is that hydrogen bonding between the N–H groups of DEED and coordinated peroxide in **A** and **B** (see above) leads to Raman inactivity of ν(O–O) in the title system. However, H_2O_2 formation was confirmed iodometrically [7, 10] on acidification of solutions of **A** in methylene chloride. The data identify **A** as a peroxocopper complex in the $[(DEED)CuBr]_2/O_2$ system.

Peroxometal complexes sometimes [33] exhibit Raman active ν(O–O) bands in the 780–880 cm^{-1} region whose frequency decreases by 25–50 cm^{-1} on substitution of ^{18}O for ^{16}O with the metal unchanged. The effects, particularly when using $^{16}O^{18}O$, are very useful in distinguishing between different peroxocomplex structures [34]. The region 900–666 cm^{-1} is where medium-to-strong N–H wagging bands are observed in the IR spectra of amines and amides [35].

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*Raman measurements are not always reliable for the identification of peroxocopper complexes [33].

We measured the KBr disk FT-IR spectra of **A**, **C** and **E** and their isotopic analogues **A***, **C*** (and **E***) made by reacting **D** with $^{18}O_2$ (and $C^{16}O_2$). Resolution was ±2 cm^{-1}. Bands at 790–802 and 860–868 cm^{-1} are observed for all these complexes and for $\mathbf{E}_{TEED}$ (L=TEED, X=Cl [32b]). Bands at 818, 818, 820, 827 and 817 cm^{-1} for **A**, **A***, **C**, **C*** and $\mathbf{E}_{TEED}$, respectively, indicate little effect of isotopic substitution. Bands at 838, 841, 846, 841 and 833 for **A**, **A***, **E**, **E*** and $\mathbf{E}_{TEED}$ reveal no evidence for the expected effects of ^{18}O substitution on IR active ν(O–O) stretching. FT-IR and Raman measurements are thus not useful for identifying peroxide in products **A** and **B**. However, chemical and kinetic data clearly indicate that **A** and **B** are peroxocopper complexes (see above and the next sections).

Kinetics of oxidation, relaxation and ultimate product formation in the [(DEED)CuBr]$_2$/O$_2$ system

Reaction of the title copper(I) dimer with O_2 proceeds in three distinct, easily resolvable steps.

Primary event

Mixing O_2 with pseudo-first-order excesses of $[(DEED)CuBr]_2$ (**D**) in methylene chloride results in large absorbance increases in the 600 nm region that are easily monitored by stopped-flow spectrophotometry. At fixed wavelength, temperature and $[O_2]$, the absorbance increase was independent of [**D**], indicating that the primary event is irreversible [23]. The absorbance increase with fixed [**D**] was accurately first-order for at least four half-lives (Fig. 3), indicating a first-order dependence of the reaction rate on $[O_2]$. At fixed temperature, the pseudo-first-order rate constant $k_{obs}(1)$ was a linear function of $[\mathbf{D}]^2$ and passed through the origin (Fig. 4), indicating irreversible rate law (7) with $k_{DL}=k_9$ as the third-order rate constant. (Detailed kinetic data are available from author G.D.) Comparison is made with our previous data [23] for the primary event in the $[(TEED)CuCl]_2/O_2$ system in Table 3.

The negative $\Delta H_9^{\ddagger}$ found in this and the previous work [23] (Table 3) strongly suggest the exothermic formation of very weak intermediate complexes **A**′ in Scheme 1, eqns. (17) and (18), with $\Delta H_9^{\ddagger} = \Delta H_{17} + \Delta H_{18}^{\ddagger} = -1.0$ kcal mol^{-1} (TEED, Cl ligands) [23] and -1.8 kcal mol^{-1} (DEED, Br). Negative $\Delta H_9^{\ddagger}$

$$\mathbf{D} + O_2 \rightleftharpoons \mathbf{A}' \qquad (17)$$

$$\mathbf{A}' + \mathbf{D} \longrightarrow \mathbf{A} \qquad (18)$$

results in decreasing k_{DL} with increasing temperature (Fig. 5). Third-order rate law (5) or (9) with this temperature dependence appears to be characteristic of $[LCuX]_2/O_2$ reactions that give tetranuclear peroxocopper complexes **A** as primary products.

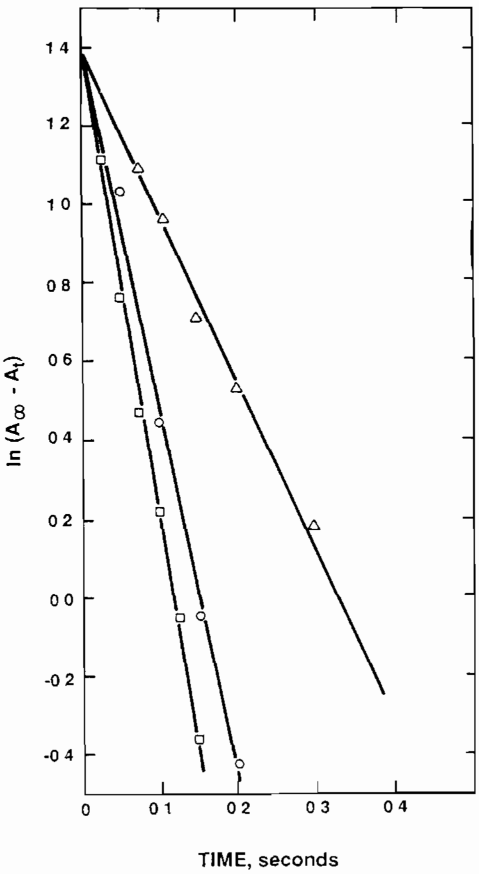

Fig. 3. First-order plots for reaction (9) of **D** (2.8 mM) with O_2 (0.44 mM) in methylene chloride at the following temperatures: −51 (□), −15.9 (○), 25.0 (△) °C. The reaction was monitored at 600 nm. Note that the observed first-order rate constant $k_{obs}(1)$ decreases with increasing temperature.

The data in Table 3 show that reaction (9) is about 80 times slower at −51 °C when the copper(I) reactant is $[(TEED)CuCl]_2$. This is largely because $\Delta H_9^{\ddagger}$ is more positive when L=TEED and X=Cl. It is important to recall that (i) $[LCuBr]_2$ dimers are oxidized *more slowly* to oxocopper(II) dimers $[LCuBr]_2O$ (eqn. (3)) with third-order rate law (5) than are the corresponding chloro complexes (see Table III of ref. 22) and (ii) that the activation enthalpies at ambient temperatures are positive in all known examples of reactions (3). Thus, the high relative rate of reaction (9) with more negative $\Delta H_9^{\ddagger}$ and the special stability of **A** and **B** with L=DEED are also due to the presence of bromide, which stabilizes the copper(I) state in the mixed valence product $[(DEED)CuBr]_4O_2$. In support of this conclusion we found that reactions (3) with reactant $[DEEDCuCl]_2$ are too rapid to be monitored by stopped-flow spectrophotometry even at −50 °C.

Relaxation of A to B

Irreversible reaction (9) is followed by exothermic, first-order relaxation of primary product **A** to a different

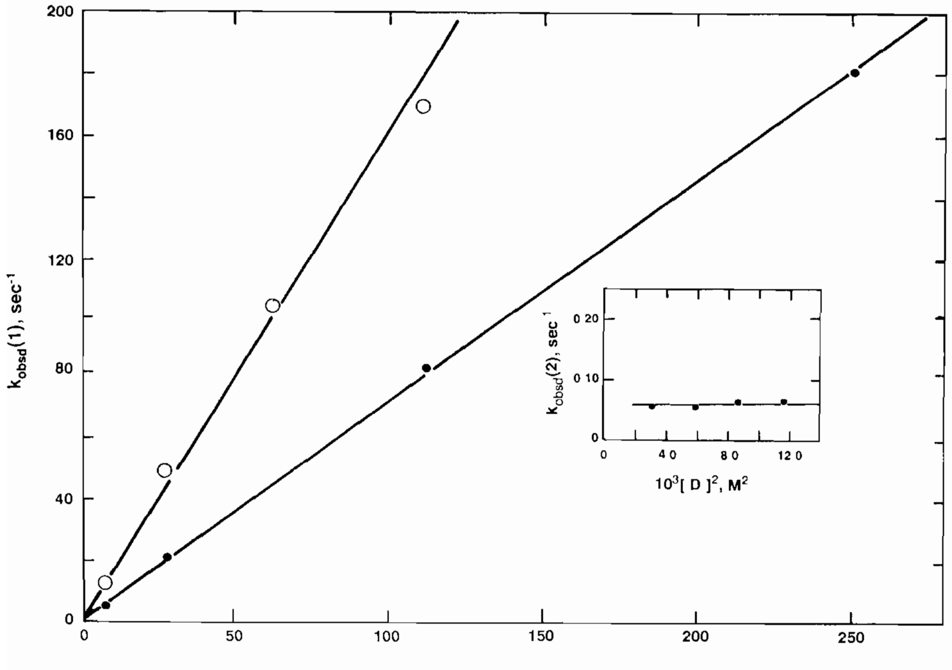

Fig. 4. Plots of $k_{obs}(1)$ vs. $[D]^2$ for reaction (9) of **D** with O_2 to form **A** in methylene chloride at −51.0 (○) and 7.7 (●) °C. Inset: plot of $k_{obs}(2)$ vs. [**A**] for relaxation (19) at −51.0 °C in methylene chloride. The monitoring wavelength is 600 nm in both cases. See Fig. 4 of ref. 23 for an example of absorbance changes accompanying primary oxidation and relaxation in the corresponding $[(TEED)CuCl]_2/O_2$ system.

TABLE 3. Kinetic data for the primary event in the reactions of $[LCuX]_2$ dimers with O_2 in methylene chloride

L,X^a	$10^{-4}\times k_9$^{b}	$\Delta H_9^{\ddagger}$^{c}	$\Delta S_9^{\ddagger}$^{d}	Reference
TEED,Cl^e	1.9	−1.0	−43	23
DEED,Br^f	148	−1.8	−38	this work

[a] Diamine and halide ligands in **D**. [b] Third-order rate constant at −51.0 °C in rate law (7) for reactions (9). Units are M^{-2} s^{-1}. [c] Units are kcal mol^{-1}. Typical error is ±0.4 kcal mol^{-1}. [d] Units are cal deg^{-1} mol^{-1} at 25 °C. Typical error is ±5 cal deg^{-1} mol^{-1}. [e] Kinetic data obtained in the temperature range −76.0 to −45.0 °C. [f] Kinetic data obtained in the temperature range −51.0 to 30.0 °C.

peroxo complex form **B** (eqn. (19), Scheme 1). Reversible reaction (19) is observed at temperatures up to *c.* −50 °C with L=TEED and X=Cl (see Fig. 4b of ref. 23).

$$\mathbf{A} \rightleftharpoons \mathbf{B},\ k_R \tag{19}$$

Similar behavior was observed in the DEED, Br system up to about −17 °C. The observed rate constant $k_{obs}(2)=k_R$ was independent of [**A**] (Fig. 4, inset) and $[O_2]$ at fixed temperature. The relaxation data at temperatures in the range −51.0 to −16.0 °C are collected with the earlier data [23] in Table 4. We see that changing the copper ligands from TEED, Cl to DEED, Br has a substantial effect on k_R, which is *c.* 40 times

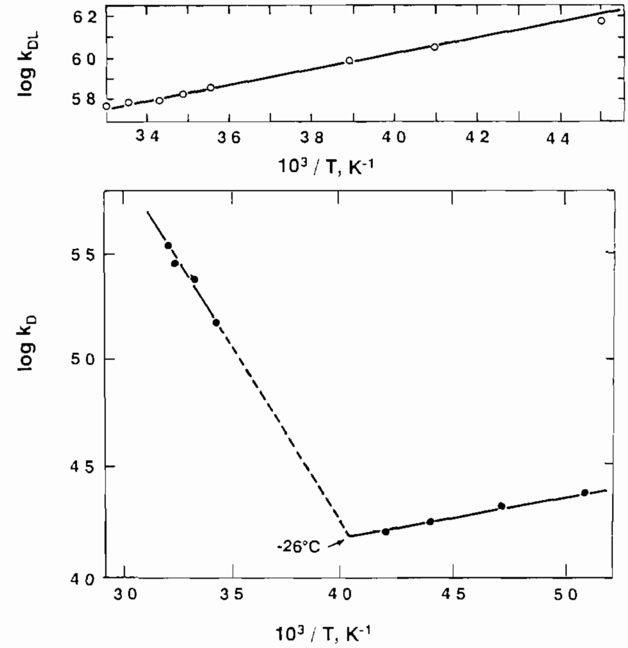

Fig. 5. Plots of log k_D or k_{DL} vs. $1/T$ for the reactions of **D** (L=TEED, X=Cl, ●) [23] and **D** (L=DEED, X=Br, ○) with O_2 in methylene chloride. See ref. 23 for discussion of the extrapolated region in the lower Figure. Note evidence for only one kinetic process over the entire temperature range in the DEED, Br system.

TABLE 4. Kinetic data for relaxation reaction (19) in methylene chloride

L,X[a]	Temp.[b]	k_R[c]	$\Delta H^{\neq}_{R}$[d]	$\Delta S^{\neq}_{R}$[e]	Reference
TEED,Cl	−76.0	0.30	0.0	−62	23
	−61.0	0.32			
	−50.1	0.30			
DEED,Br	−51.0	0.007	7.5	−6	this work
	−40.0	0.018			
	−29.0	0.036			
	−21.0	0.055			
	−16.0	0.072			

[a]Ligands in **A** and **B**. [b]Given in °C. [c]Units are s^{-1}. [d]Units are kcal mol^{-1}. [e]Units are cal deg^{-1} mol^{-1} at 25 °C.

TABLE 5. Kinetic data for conversion of **A** to **C** in methylene chloride

L,X[a]	$10^5 \times k_8$[b]	$t_{1/2,8}$[c]	$\Delta H^{\neq}_{8}$[d]	$\Delta S^{\neq}_{8}$[e]	Reference
TEED,Cl	1.8×10^8[f]	0.40[g]	25.0[f]	40[f]	23
DEED,Br	8.9	3.2[h]	14.8	−28	this work

[a]Ligands in **A**. [b]Units are s^{-1} at 25 °C. [c]Half-life of **A** at 25 °C. [d]Units are kcal mol^{-1}. Typical error is ±0.4 kcal mol^{-1}. [e]Units are cal deg^{-1} mol^{-1} at 25 °C. Typical error is ±5 cal deg^{-1} mol^{-1}. [f]Estimated (see ref 23). [g]Units are ms. [h]Units are h.

lower near −50 °C. The larger activation enthalpy with DEED and Br ligands confirms that they stabilize **A**.

Conversion of A to C

The decomposition of $[(DEED)CuBr]_4O_2$ (**A**) to ultimate oxidation product $[(DEED)CuBr]_2O$ (**C**, eqn. (8)) is slow and was easily monitored by conventional spectrophotometry at 450 nm in the Lambda 4B instrument. Plots of $\ln(A_\infty - A_t)$ versus time, where A_t is the absorbance at fixed wavelength at time t, were accurately linear for at least four half-lives, indicating that reaction (8) is first-order, with rate constant $k_{obs}(3) = k_8$. The first-order rate constants were independent of monitoring wavelength, [**A**] and the presence of O_2, eliminating the possibility that they refer to oxidation of DEED and confirming the manometric measurements of reactions (8) and (9). The data are compared with those for the TEED, Cl system in Table 5.

At 21 °C, peroxo complex **A** decomposes about 20 million times more slowly than the corresponding complex with TEED and Cl ligands [23]. The much longer half-life of **A** (L = DEED, X = Br) is due to compensation of the lower $\Delta H^{\neq}_{8}$ by a much more negative $\Delta S^{\neq}_{8}$ in the $[(DEED)CuBr]_4O_2 \rightarrow [(DEED)CuBr]_2O$ reaction. The more negative $\Delta S^{\neq}_{8}$ indicates that the activated complex for reaction (8) is much tighter with L = DEED and X = Br. Factors likely to be responsible for this are (i) the need for stronger bonding of peroxide to Cu^IBr than to Cu^ICl centers in **A** so that the crucial third electron can be transferred from copper(I) to break the O–O bond (Scheme 1) and (ii) hydrogen-bonded assistance from the N–H groups of DEED in this process.

Conclusions

Depending on the circumstances, polynuclear copper(I) complex–dioxygen reactions can result in the transfer of up to four electrons to O_2. Activated complex assembly or any one of these transfers may be rate-determining. This is why we still do not fully understand the stability or otherwise of natural [11] or synthetic [6–11, 23] peroxocopper complexes. However, peroxide cannot tolerate an added electron and we can appreciate that intermolecular (eqn. (16)) or intramolecular (eqn. (9)) electron transfer from copper(I) to peroxide has specific kinetic requirements that vary with the ligands and experimental temperature. Our work suggests that resistance to total O_2 reduction may be found in systems where copper(I) is stabilized (here by bromide) and bound peroxide is involved in hydrogen bonding with copper ligands. This hydrogen bonding must be delicately balanced if the copper ligand is to be oxidatively stable [16, 20, 22, 28, 29] because oxocopper(II) complexes like $[LCuX]_2O$ are strong protic bases [13, 19–21, 24].

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