4730 *Inorg. Chem.* **1990**, *29*, 4730–4735

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Products and Kinetics of the Oxidation of Neutral Dimeric Iodo(*N*,*N*,*N*′,*N*′-tetraalkyl diamine)copper(I) Complexes $[LCuI]_2$ by Dioxygen in Nitrobenzene

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Received May 22, 1990

Copper(I) iodide dissolves in methylene chloride and nitrobenzene solutions of equimolar diamine ligands L = *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMED), *N*,*N*,*N*′,*N*′-tetraethylethylenediamine (TEED), *N*,*N*,*N*′,*N*′-tetrapropylethylenediamine (TPED), and *N*,*N*,*N*′,*N*′-tetramethyl-1,3-propanediamine (TMPD) under dinitrogen to give neutral dimeric copper(I) molecules $[LCuI]_2$. These dimers rapidly react with dioxygen to give oxocopper(II) products $[LCuI]_2O$, which appear from spectral comparisons to contain five-coordinate copper(II). Dimers $[LCuI]_2O$ react with carbon dioxide in methylene chloride and nitrobenzene to form the respective (carbonato)copper(II) complexes $[LCuI]_2CO_3$. The cryoscopic properties and electronic and EPR spectra of $[LCuI]_2CO_3$ indicate the presence of five-coordinate copper(II) in dimeric molecules with asymmetrical carbonato bridges, a cis arrangement of terminal iodo ligands, or both of these structural features. Kinetic studies of the oxidation of excess $[LCuI]_2$ with dioxygen in nitrobenzene reveal a rate law that is first-order in $[[LCuI]_2]$ and first-order in $[O_2]$. This contrasts sharply with previous results for oxidations of $[LCuX]_2$ dimers (X = Cl, Br) by dioxygen, which are second-order in $[[LCuX]_2]$. Comparison of data for second-order oxidations of copper(I) complexes $[NCuX]_4$, $[NCuX]_4Y$, and $[LCuI]_2$ by dioxygen, where N is a monodentate pyridine and Y is 3,4,5,6-tetrachlorocatecholate, indicates a mechanism of $[LCuI]_2$ oxidation that apparently requires rate-determining penetration of their Cu(I,I)Cu cores by the dioxygen molecule.

Introduction

Complexes formed between copper(I) halides and amines are of continuing interest because of their useful catalytic[2] and photoemissive[3] properties. A growing body of data reveals their variety of molecular copper(I) geometries and a tendency toward the formation of halo-bridged polymers in the solid state.[4] However, discrete halo-bridged dimers $[LCuX]_2$ and tetramers $[NCuX]_4$ are formed in weakly coordinating aprotic solvents like methylene chloride and nitrobenzene when L is a bidentate amine, N is a monodentate pyridine, X is Cl or Br, and the molar amine:copper ratio *R* is 1.[5] Halo(amine)copper(I) chemistry thus provides ready access to a variety of polymetallic molecules. These molecules are multielectron reducing agents.[2,5]

The dioxygen sensitivity of solid copper(I) halides decreases as the halide is changed from chloride to bromide to iodide.[4] It is accelerated by light and by the coordination of saturated amines[5b–d] or pyridines.[2g,5a] Most of the available structural[4] and photoemissive[3] data on halo(amine)copper(I) complexes refer to the iodides because of their relative air stability. Air oxidation of iodo(amine)copper(I) complexes is an important consideration because any formation of copper(II) centers might quench their photoemissive and semiconducting properties.[3,4]

Previous kinetic studies of the oxidation of halo(amine)copper(I) complexes by dioxygen in aprotic solvents have employed the chlorides and bromides because of higher solubilities and copper(I) oxidation rates than for the iodides.[5] However, the halide is known to affect the catalytic efficiency and specificity of halo(amine)copper(I) complexes,[2] in part because of these variations in copper(I) oxidation rate.[5b] There is an obvious need for more information on the reactions of iodo(amine)copper(I) complexes with dioxygen.

Table I. Analytical and Cryoscopic Data for $[LCuI]_2Y$ Complexes (Y = O, CO_3)

L	Y	anal., %[a] C	H	N	Cu	M_r[b]
TMED						600 ± 30 (613)
	O				20.5 (20.2)	600 ± 30 (629)
	CO_3	23.4 (23.2)	4.5 (4.8)	8.1 (8.3)	18.3 (18.9)	700 ± 30 (673)
TEED						700 ± 30 (725)
	O				17.8 (17.1)	750 ± 30 (741)
	CO_3	31.9 (32.1)	6.2 (6.1)	7.2 (7.1)	16.6 (16.1)	800 ± 30 (785)
TPED						800 ± 30 (837)
	O				15.4 (14.9)	900 ± 30 (853)
	CO_3	38.4 (38.8)	7.2 (7.1)	6.3 (6.2)	13.8 (14.2)	870 ± 30 (897)
TMPD						620 ± 30 (641)
	O				19.1 (19.3)	700 ± 30 (657)
	CO_3	25.5 (25.7)	5.0 (5.1)	7.8 (8.0)	18.6 (18.1)	700 ± 30 (701)

[a] Calculated values in parentheses. See text for elemental analytical considerations for $[LCuI]_2$ and $[LCuI]_2O$ samples. [b] Measured cryoscopically in nitrobenzene at the (3–5) × 10^{-2} M level. The freezing point of nitrobenzene is 5.00 °C, and its freezing point depression constant is 7.00 °C/*ml*.[5a]

This paper reports the products and kinetics of oxidation of excess dimeric copper(I) complexes $[LCuI]_2$ by dioxygen in nitrobenzene. Here, L are the familiar bidentate ligands *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMED), *N*,*N*,*N*′,*N*′-tetraethylethylenediamine (TEED), *N*,*N*,*N*′,*N*′-tetrapropylethylenediamine (TPED), and *N*,*N*,*N*′,*N*′-tetramethyl-1,3-propanediamine (TMPD). The products are shown to be the respective neutral dimeric oxoiodocopper(II) complexes $[LCuI]_2O$, which react with

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(1) (a) Alexandria University. (b) Northeastern University.

(2) (a) Hay, A. S.; Blanchard, H. F.; Endres, G. F.; Eustance, J. W. *J. Am. Chem. Soc.* **1959**, *81*, 6335. (b) Endres, G. F.; Hay, A. S.; Eustance, J. W. *J. Org. Chem.* **1963**, *28*, 1300. (c) Hay, A. S. *Adv. Polym. Sci.* **1967**, *4*, 496. (d) Hay, A. S. *Polym. Eng. Sci.* **1976**, *16*, 1. (e) Hay, A. S.; Shenian, P.; Gowan, A. C.; Erhardt, P. F.; Haaf, W. R.; Therberg, J. E. *Encyclopedia of Polymer Science and Technology*; Interscience: New York, 1969; p 92. (f) Finkbeiner, H. L.; Hay, A. S.; White, D. M. Polymerization by Oxidative Coupling. In *Polymerization Processes*; Schildnecht, C. E., Skeist, I., Eds.; Wiley-Interscience: New York, 1977; p 537 and references therein. (g) Davies, G.; El-Sayed, M. A. Homogeneous Oxidative Coupling Catalysts. In *Copper Coordination Chemistry: Biochemical and Inorganic Perspectives*; Karlin, K. D., Zubieta, J. A., Eds.; Adenine Press: Guilderland, NY, 1983; p 281.

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Table II. EPR and Electronic Spectral Data for $[LCuI]_2Y$ Products ($Y = O, CO_3$) in Aprotic Solvents

			EPR[a]					
L	Y	temp, K	$A_\parallel$	$g_\parallel$	$g_\perp$	$g(\Delta M_s \pm 2)$	g_i	λ_{max}, nm[b] (ϵ_λ, $M^{-1}\ cm^{-1}$)
TMED	O	300						435 (810), 600 (130)
	CO_3	300					2.01	435 (1090), 700 (190)
		25	140	2.25	1.99	3.5		
TEED	O	300						430 (1100), 640 (140)
	CO_3	300					2.07	435 (1120), 700 (140)
	CO_3	25	160	2.20	1.96	3.6		
TPED	O	300						425 (960), 625 (80)
	CO_3	300					2.08	425 (1100), 700 (150)
	CO_3	25	180	2.18	1.97	3.7		
TMPD	O	300						480 (1100), 450 (1140), 650 (240)
	CO_3	300					2.12	435 (990), 435 (1140), 700 (110)
	CO_3	25	110	2.15	2.01	3.7		

[a] In methylene chloride. [b] In nitrobenzene. [c] Units are 10^{-4} cm^{-1}.

CO_2 to form the corresponding neutral carbonates $[LCuI]_2CO_3$. Although the rate law for oxidations of excess $[LCuX]_2$ (X = Cl, Br) by dioxygen is first-order in $[O_2]$ and second-order in $[[LCuX]_2]$,[5b–d] we now report that the corresponding reactions with X = I are first-order in $[[LCuI]_2]$. The kinetic data are compared with those for other second-order halo(amine)copper(I)–dioxygen reactions in aprotic solvents.

Experimental Section

Materials. Copper(I) iodide was prepared by the literature method[6] and stored in a desiccator in the dark. Nitrobenzene was distilled under reduced pressure from P_2O_5 and stored over 4-Å molecular sieves. Methylene chloride was purified as described previously.[5] High-purity dinitrogen was deoxygenated by passage through a column of Alfa DEOX solid catalyst. Ligands L (Ames Laboratories or Aldrich) were distilled under reduced pressure immediately before use.

Synthesis of Reactants $[LCuI]_2$. Solutions of the respective L (2.50 mmol) in nitrobenzene (25 mL) under dinitrogen were treated with copper(I) iodide (2.50 mmol) at room temperature. The mixtures were stirred under dinitrogen until clear solutions were obtained. No serious attempt was made to isolate the product copper(I) complexes as solids: representative samples gave irreproducible elemental analyses because of their marked air sensitivity. However, conductance and cryoscopic measurements[5a] on their nitrobenzene solutions confirm[7] that they contain discrete neutral dimeric copper(I) complexes $[LCuI]_2$ (Table I).

Dioxygen Uptake Measurements. The consumption of dioxygen by the nitrobenzene solutions of $[LCuI]_2$ from the previous section was monitored by standard Warburg manometry[5a] at room temperature. Reaction with stoichiometry $\Delta[[LCuI]_2]/\Delta[O_2] = 2.0 \pm 0.1$ was generally complete in less than 3 h. This stoichiometry is consistent with complete reduction of dioxygen and oxidation of copper(I) to copper(II) to give products $[LCuI]_2O$ on the time scale of our kinetic measurements (see below).[8]

Oxidation Products. The products of oxidation of methylene chloride solutions of $[LCuI]_2$ by dioxygen in the absence and presence of excess carbon dioxide were isolated as solids by solvent evaporation. Products $[LCuX]_2O$ (X = Cl, Br) are highly reactive: they polymerize on standing in dinitrogen and suffer oxidation of L in the presence of dioxygen.[5] Therefore, we immediately analyzed solid products $[LCuI]_2O$ for copper by inductively coupled plasma spectroscopy after standard sample preparation, as described previously.[5] We do not have in-house C,H,N analytical capability and sent the solid oxocopper(II) products $[LCuI]_2O$ to Desert Analytical Services, Tucson, AZ, for C,H,N analysis. Poor reproducibility of C,H,N analytical data for duplicate samples of the same product indicated deterioration of the samples on shipping (under dinitrogen) and handling. This accounts for the lack of C,H,N data for $[LCuI]_2O$ products in Table I. However, no analytical problems were encountered with carbonato derivatives $[LCuI]_2CO_3$.

Analytical and cryoscopic data for the respective neutral dimeric products $[LCuI]_2O$ and $[LCuI]_2CO_3$ are collected in Table I. Attempted growth of single crystals of these solid products with a variety of techniques was unsuccessful.[8]

Physical Measurements. The electronic spectra of products $[LCuI]_2O$ and $[LCuI]_2CO_3$ in nitrobenzene (Table II) were measured under dinitrogen with Beckman DK-1A and DB-G spectrophotometers in matched quartz cells at room temperature. EPR spectra of 1.0 mM solutions of these complexes in methylene chloride were recorded at 100 kHz and at 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 at 25 K.

Kinetic measurements of oxidation reactions 10 were made by monitoring absorbance increases as a function of time at fixed wavelength in the region 550–700 nm by conventional spectrophotometry. Reductants $[LCuI]_2$ were always present in pseudo-first-order excess. The total reactant concentration range was $[[LCuI]_2]_0 = (11.7–31.7) \times 10^{-3}$ M, with $[O_2]_0 = 4.4 \times 10^{-4}$ M. Temperature was controlled to ±0.05 °C in the range 18.0–60.0 °C. Pseudo-first-order rate constants k_{obsd} were obtained from the slopes of linear plots of log $(A_\infty - A_t)$ vs time, where A_t is the absorbance at fixed wavelength and temperature at time t. Each run was repeated at least four times under fixed experimental conditions to establish an upper limit of ±5% for each reported rate constant.

Results and Discussion

General Observations. Copper(I) and copper(II) probably have the most extensive amine coordination chemistry of all the transition-metal ions. This is due to their lability, their high affinity for amines, and the wide variety of ligand geometries that both copper oxidation states can accommodate.[4]

Strong interest in the solid-state and solution chemistry of copper(I) complexes is due to their interesting photoemissive properties[3] and a longstanding recognition that most copper-catalyzed oxidation reactions are initiated by the copper(I) state.[2,10]

A recent survey[4b] indicates the prevalence of the $[LCuX]_2$ rhombohedron in the structural chemistry of halo(diamine)copper(I) complexes. These units either exist as discrete entities or are linked together in the solid state to form tetramers or higher polymers with a variety of repeat units. The solid-state structures seem to depend on the amine ligand, its steric demands, the molar amine:copper ratio, and the manner in which single crystals are obtained.[4b]

Our work is concentrated on the catalytic properties of complexes formed between copper(I) halides and simple, industrially important amines at low molar amine:copper(I) ratios in aprotic solvents. Particular sterically unhindered pyridines (pyridine, *N,N*-diethylnicotinamide, ethyl nicotinate (N))[2g,5a,11] and *N,N,N',N'*-tetraalkyl diamines (L)[5b–d] solubilize copper(I) halides in aprotic solvents, promote their aprotic oxidation by dioxygen, and are at least moderately oxidatively stable as ligands in the products.[5,8,11]

A variety of solid-state[4] and solution-phase[5a,11] evidence indicates that the above monodentate ligands N favor the formation of cubanes $[NCuX]_4$ as discrete molecular units. These units are

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(6) Keller, R. N.; Wycoff, H. D. *Inorg. Synth.* **1946**, *2*, 1.

(7) Haitko, D. A.; Garbauskas, M. F. In *Biological and Inorganic Copper Chemistry*; Karlin, K. D., Zubieta, J., Eds.; Adenine Press: Guilderland, NY, 1986; Vol. 2, p 77.

(8) The *N*-alkyl substituents of $[LCuX]_2$ complexes are subject to slow oxidation by excess dioxygen, as indicated by consumption of more dioxygen than is required for the stoichiometric oxidation of copper(I) to copper(II).[5b,c,9] However, such ligand oxidation is much slower than reactions 1, which refer to copper(I) oxidation.

(9) Thompson, J. S. In ref 7, p 1.

(10) Glaser, C. *Chem. Ber.* **1869**, *2*, 422; *Ann. Chem. Pharm.* **1870**, *154*, 159.

(11) El-Sayed, M. A.; Abu-Raqabah, A.; Davies, G.; El-Toukhy, A. *Inorg. Chem.* **1989**, *28*, 1909. Abu-Raqabah, A. Doctoral Dissertation, Northeastern University, 1987.

held together by copper–halide bonds, and the geometry of the donor atoms is close to tetrahedral. The core of each cubane is a tetrahedron of halogen atoms.

On the other hand, ligands L favor the rhombohedron $[LCuX]_2$ as discrete dimeric units,[4,7,12] which can be thought of as half of the corresponding cubane. This cubane dissociates into dimers because L is bidentate and copper prefers tetrahedral four-coordination.[4,5b–d,7,12]

Halo(amine)copper(I) complexes $[NCuX]_4$ and $[LCuX]_2$ (X = Cl, Br) rapidly reduce dioxygen in aprotic solvents.[2g,5,11] The driving force for these exothermic copper(I) oxidation reactions is the formation of strong oxo–copper(II) bonds. Kinetic studies show that the observed rate laws are a direct reflection of the reductant molecularity (eqs 1–4), undoubtedly because of the marked tendency for complete dioxygen reduction and the formation of oxocopper(II) products.[2g,5,11]

$$[NCuX]_4 + O_2 \rightarrow [NCuX]_4O_2 \qquad (1)$$

$$d[[NCuX]_4O_2]/dt = k_T[[NCuX]_4][O_2] \qquad (2)$$

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

$$d[[LCuX]_2O]/dt = k_D[[LCuX]_2]^2[O_2] \qquad (4)$$

Comparison of kinetic data for oxidation of a variety of coppper(I) cubanes $[N_nCuX]_4$ (n = 1, 2; X = Cl, Br) and their transmetalated derivatives[13–15] indicates insertion of the dioxygen molecule into the halo core as the rate-determining step.[2g,5a,11,14,15] The corresponding slow step in reactions 3 appears to be assembly of the respective activated complexes.[5b–d] Decreasing rates with increasing length of the *N*-alkyl substituents of L indicate steric barriers to the assembly of activated complexes containing two $[LCuX]_2$ units and one O_2 molecule prior to rapid electron transfer. Especially strong driving forces for electron transfer are presumably due to the marked preference of copper(II) for hard amine ligands like L. In any event, electron transfer from copper(I) to dioxygen is very much faster than either of the rate-determining steps of reactions 1 and 3.[5,11]

The protic basicity of the oxocopper(II) products of eqs 1 and 3 is very important in determining whether or not they will initiate the oxidation of protic substrates.[2g,5,11,16] It depends on whether the amine ligand is mono- or bidentate, on whether it is relatively hard or soft, and on the disposition of the oxo groups.[2g,5a,11,16] A clue to the disposition of oxo groups in oxocopper(II) complexes is the observation that some of them react with carbon dioxide to form (carbonato)copper(II) products (eqs 5 and 6).[2g,5,11,16–18]

$$[NCuX]_4O_2 + 2CO_2 \rightarrow [NCuX]_4(CO_3)_2 \qquad (5)$$

$$[LCuX]_2O + CO_2 \rightarrow [LCuX]_2CO_3 \qquad (6)$$

This suggests the existence of reactant Cu–O–Cu units whose bridging angles can be opened to accommodate the linear Cu–O–Cu arrangement in the carbonato products.[17,18]

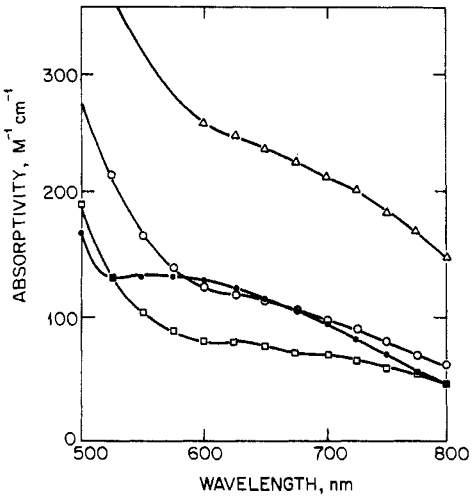

Figure 1. Electronic spectra of $[LCuI]_2O$ complexes in nitrobenzene at 25 °C. The ligands L are as follows: TMPD, △; TEED, ○; TPED, □; TMED, ●.

The preceding chemistry has almost entirely been restricted to amine complexes made from copper(I) chloride and bromide because of their relative dioxygen sensitivity and the known catalytic properties of the oxidation products.[2,5,11,16–18] Iodide preferentially stabilizes copper(I),[19] and the cubanes $[NCuI]_4$ are air-stable and noncatalytic.[2g,17] However, we recently discovered that $[NCuI]_4$ (N = *N,N*-diethylnicotinamide) is rapidly oxidized by 3,4,5,6-tetrachloro-1,2-benzoquinone Cl_4BQ and that the mixed-valence product of reaction 7 (Y is 3,4,5,6-tetrachlorocatecholate) reacts with dioxygen in eq 8.[20] We found that reaction 8 is governed by second-order rate law 9,[20] which is in

$$[NCuI]_4 + Cl_4BQ \rightarrow [NCuI]_4Y \qquad (7)$$

$$[NCuI]_4Y + \tfrac{1}{2}O_2 \rightarrow [NCuI]_4Y(O) \qquad (8)$$

$$d[[NCuI]_4Y(O)]/dt = k_9[[NCuI]_4Y][O_2] \qquad (9)$$

sharp contrast with third-order rate law 4 for reactions 3.[5b–d,21] This observation and the lack of oxidation data for iodo(amine)copper(I) complexes prompted us to examine the aprotic oxidation of $[LCuI]_2$ complexes by dioxygen, particularly because there is a good deal of structural information on the reactants.

Reactant Structures. Haitko and Garbauskas have reported molecular structures for a range of $[LCuI]_2$ complexes.[7] They exist as discrete iodo-bridged molecules LCu(I,I)CuL, with almost perfect tetrahedral geometry about copper(I) and Cu···Cu separations ranging from 2.58 to 2.73 Å, depending on the diamine ligand. The Cu···Cu separations for two of the reactants of this study, $[(TMED)CuI]_2$ and $[(TEED)CuI]_2$, are 2.58 and 2.66 Å, respectively.[7] This information may be pertinent to understanding their oxidation mechanisms (see below).

Oxocopper(II) Products. Dioxygen uptake measurements and the cryoscopic and analytical data in Table I indicate that the products of oxidation of $[LCuI]_2$ complexes by dioxygen in methylene chloride and nitrobenzene are discrete molecules $[LCuI]_2O$ (eq 10). These products are only moderately stable

$$2[LCuI]_2 + O_2 \rightarrow 2[LCuI]_2O \qquad (10)$$

as solids, and attempted growth of single crystals results in decomposition.[8]

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(12) Churchill, M. R.; Davies, G.; El-Sayed, M. A.; Fournier, J. A.; Hutchinson, J. P.; Zubieta, J. A. *Inorg. Chem.* **1984**, *23*, 783.

(13) $[NCuX]_4$ molecules (X = Cl, Br) are monotransmetalated by $M(NS)_2$ and $Co(NS)_3$ reagents (M = Co, Ni, Cu, Zn; NS = monoanionic *S*-methyl isopropylidenehydrazinecarbodithioate) to give $N_3Cu_3M(NS)X_4$[14] and $N_3Cu_3Co(NS)_2X_4$[15] products, respectively. These products are oxidized to $N_3Cu_3MX_4O_2$ molecules by dioxygen with a second-order rate law analogous to eq 2. The kinetic data are consistent with rate-determining insertion of dioxygen into the halo cores of $N_3Cu_3M(NS)X_4$[14] and $N_3Cu_3Co(NS)_2X_4$.[15] Data for these oxidation reactions are included in the correlation of activation parameters for second-order oxidation in Figure 6.

(14) Davies, G.; El-Sayed, M. A.; El-Toukhy, A.; Gilbert, T. R.; Nabih, K. *Inorg. Chem.* **1986**, *25*, 1929.

(15) Davies, G.; El-Sayed, M. A.; El-Toukhy, A.; Henary, M.; Gilbert, T. R. *Inorg. Chem.* **1986**, *25*, 2373.

(16) Davies, G.; El-Sayed, M. A.; El-Toukhy, A.; Henary, M.; Martin, C. A. *Inorg. Chem.* **1986**, *25*, 4479.

(17) Churchill, M. R.; Davies, G.; El-Sayed, M. A.; Hutchinson, J. P. *Inorg. Chem.* **1982**, *21*, 1002.

(18) (a) Churchill, M. R.; Davies, G.; El-Sayed, M. A.; El-Shazly, M. F.; Hutchinson, J. P.; Rupich, M. W.; Watkins, K. O. *Inorg. Chem.* **1979**, *18*, 2296. (b) Churchill, M. R.; Davies, G.; El-Sayed, M. A.; El-Shazly, M. F.; Hutchinson, J. P.; Rupich, M. W. *Inorg. Chem.* **1980**, *19*, 201.

(19) Addison, A. W.; Rao, T. N.; Sinn, E. *Inorg. Chem.* **1984**, *23*, 1957. Patterson, G. S.; Holm, R. H. *Bioinorg. Chem.* **1975**, *4*, 257.

(20) Davies, G.; El-Sayed, M. A. *Inorg. Chem.*, in press.

(21) The point of comparison here is that mixed-valence molecules $[NCuX]_4Y$, which contain two formal copper(I) centers (Y = 3,4,5,6-tetrachlorocatecholate)[20] can be considered to be formal copper(I) dimers in their reactions with dioxygen.[20]

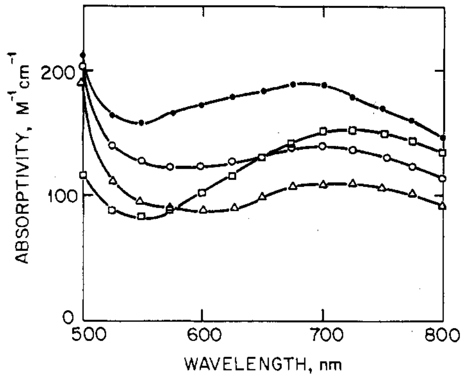


Figure 2. Electronic spectra of $[\mathrm{LCuI}]_2\mathrm{CO}_3$ complexes in nitrobenzene at 25 °C. The ligands L are as follows: TMED, ●; TEED, ○; TMPD, △; TPED, □.

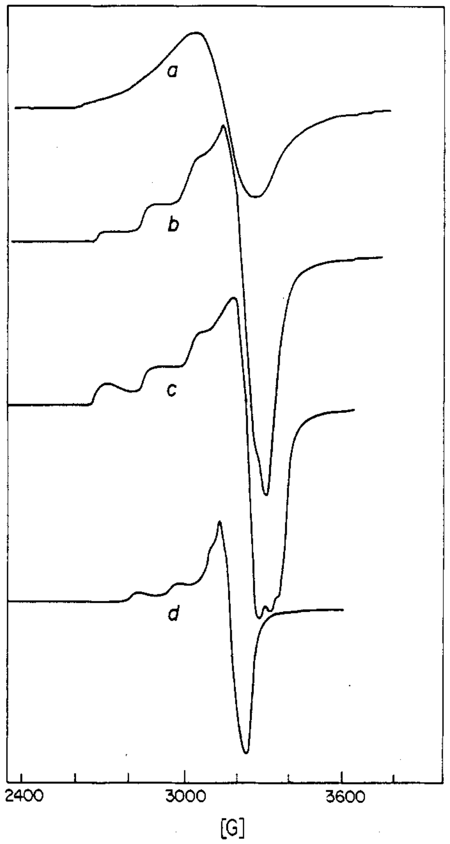
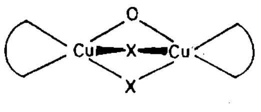


Figure 3. EPR spectra of $[\mathrm{LCuI}]_2\mathrm{CO}_3$ complexes (1.0 mM) in methylene chloride at 25 K. The ligands L are as follows: (a) TMED; (b) TEED; (c) TPED; (d) TMPD.

Their electronic spectra in nitrobenzene (Table II and Figure 1) exhibit weak, broad bands with poorly defined maxima in the region 600–640 nm. The spectra of the corresponding chloro and bromo complexes contain similar broad bands of higher intensity at longer wavelength.[22] The following triply bridged dimeric core structure for $[\mathrm{LCuX}]_2\mathrm{O}$ complexes is consistent with their spectroscopic properties:[5b,12]



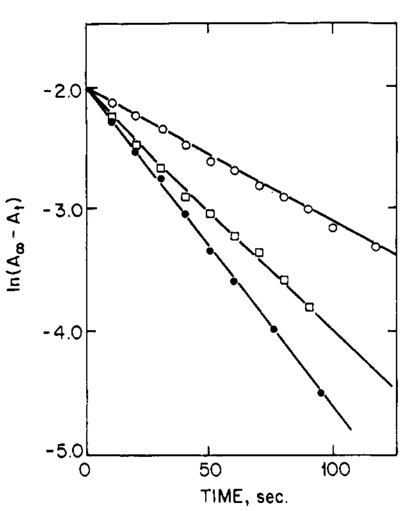


Figure 4. First-order kinetic plots for the reaction of excess $[(\mathrm{TMED})\mathrm{CuI}]_2$ with dioxygen at 21.0 °C in nitrobenzene. The initial concentrations $[[(\mathrm{TMED})\mathrm{CuI}]_2]_0$ (mM) are as follows: 11.7, ○; 21.1, □; 31.7, ●. The slope of each line gives the respective first-order rate constant k_{obsd}.

Table IV. Kinetic Data for Oxidation of Excess Dimeric Complexes $[\mathrm{LCuI}]_2$ by Dioxygen in Nitrobenzene (Reactions 10, Rate Law 13)

L	k_{13}[a]	ΔH_{13}^{*}[b]	ΔS_{13}^{*}[c]
TMPD	6.9	7.3	-30
TMED	1.0	9.5	-27
TEED	1.6	14.0	-11
TPED	4.8	6.2	-35

[a] Units are M^{-1} s^{-1} at 25 °. [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}.

(Carbonato)copper(II) Derivatives. The analytical and cryoscopic data in Table I indicate that reacting the products of reactions 10 with excess carbon dioxide results in the formation of discrete, dimeric (carbonato)copper(II) molecules $[\mathrm{LCuI}]_2\mathrm{CO}_3$ (eq 11). The same products are obtained by running reactions 10 in the presence of excess carbon dioxide (eq 12).

$$[\mathrm{LCuI}]_2\mathrm{O} + \mathrm{CO}_2 \rightarrow [\mathrm{LCuI}]_2\mathrm{CO}_3 \quad (11)$$

$$2[\mathrm{LCuI}]_2 + \mathrm{O}_2 + 2\mathrm{CO}_2 \rightarrow 2[\mathrm{LCuI}]_2\mathrm{CO}_3 \quad (12)$$

The electronic spectra of the $[\mathrm{LCuI}]_2\mathrm{CO}_3$ products are summarized in Table II and illustrated in Figure 2. We observe weak[23] but better defined absorption bands at longer wavelength than for the corresponding oxo complexes $[\mathrm{LCuI}]_2\mathrm{O}$ (Figure 1). Such spectra are characteristic of (amine)copper(II) complexes containing fewer than three halo ligands per copper(II) center.[24] This indicates five-coordination in $[\mathrm{LCuI}]_2\mathrm{CO}_3$.[17,18]

The EPR spectra of $[\mathrm{LCuI}]_2\mathrm{CO}_3$ in methylene chloride are isotropic (Table II). Cooling the solutions to 25 K results in classical axial spectra ($g_\parallel > g_\perp$) (Figure 3) that indicate a $d_{x^2-y^2}$ ground state and distorted square-pyramidal geometry about copper(II).[18] All the products exhibit a weak resonance at $g = 3.50–3.72$ ($\Delta M_s \pm 2$, Table II) that is expected for dimeric structures containing magnetically coupled copper(II) centers.[18]

Single crystals have been obtained for some products of reactions 6.[17,18] $[(\mathrm{TEED})\mathrm{CuCl}]_2\mathrm{CO}_3$ contains a planar, asymmetrical carbonato bridging system with a cis arrangement of terminal chloro ligands and is EPR active,[18b] while $[(\mathrm{TMPD})\mathrm{CuCl}]_2\mathrm{CO}_3$ contains a symmetrical carbonato bridge and a trans-chloro ligand arrangement.[18a] The latter complex and the corresponding bromide are diamagnetic and EPR silent. The origins of these structural preferences are not understood. It is especially interesting to find that changing the halide from chloride or bromide

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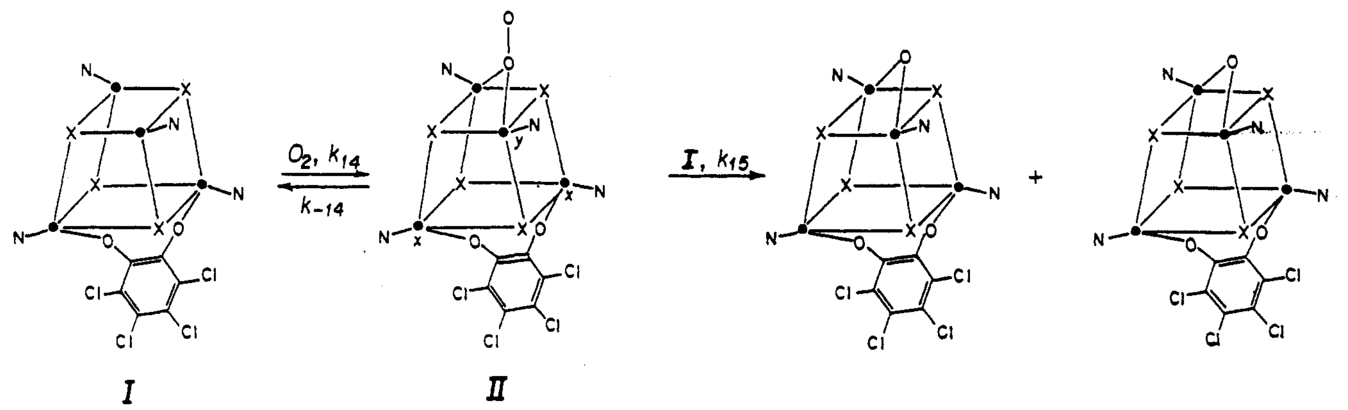
[22] Representative comparative spectral data for $[\mathrm{LCuX}]_2\mathrm{O}$ dimers are as follows. With L = TEED, absorption maxima are observed at 675 nm (ϵ 228 M^{-1} cm^{-1}), 700 (265), and 640 (140) for X = Cl,[5b] Br,[12] and I (Table II), respectively.

[23] Representative comparative spectral data for $[\mathrm{LCuX}]_2\mathrm{CO}_3$ dimers are as follows. With L = TEED, absorption maxima are observed at 760 nm (ϵ 285 M^{-1} cm^{-1}), 710 (320), and 700 (140) for X = Cl,[5b] Br,[15b] and I (Table II), respectively.

[24] Davies, G.; El-Toukhy, A.; Onan, K. D.; Veidis, M. *Inorg. Chim. Acta* **1985**, *98*, 85.

Scheme I



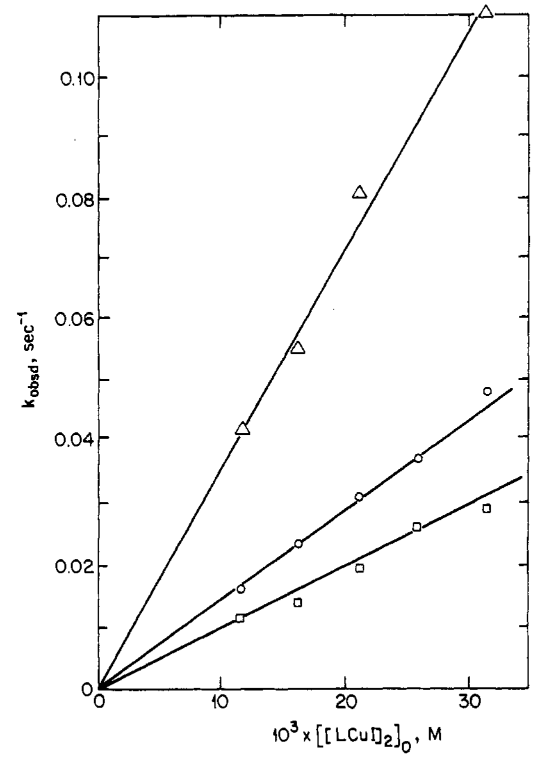


Figure 5. Plot of k_{obsd} vs $[[LCuI]]_0$ for the reactions of excess $[LCuI]_2$ dimers with dioxygen in nitrobenzene. The ligands L and the experimental temperatures are as follows: TPED (18.0 °C), △; TEED (20.0 °C), ○; TMED (21.0 °C), □. The slopes of these plots give the respective second-order rate constants k_{13} (M^{-1} s^{-1}).

to iodide in reactions 6 (that is, to give reaction 11) results in EPR-active (carbonato)copper(II) products even when L = TMPD. We conclude from their EPR activity that the products of reactions 11 and 12 contain asymmetrical carbonato bridges, a cis arrangement of their terminal iodo ligands, or both of these structural features.[17,18]

Kinetics of Oxidation of $[LCuI]_2$ Complexes by Dioxygen in Nitrobenzene. Reactions 10 in nitrobenzene result in absorbance increases in the 550–700-nm region that are easily monitored by conventional spectrophotometry. The reactions were studied with a large excess of $[LCuI]_2$ to ensure complete dioxygen reduction and pseudo-first-order conditions. Experiments are fixed wavelength, temperature, and $[[LCuI]_2]_0$ gave first-order plots that were linear to at least 4 half lives and exhibited no evidence for reactant preassociation (Figure 4). This indicates that reactions 10 are first-order in $[O_2]$. Plots of the pseudo-first-order rate constants k_{obsd} at fixed temperature vs $[[LCuI]_2]_0$ were linear and passed through the origin (Figure 5). This indicates irreversible reactions 10 with second-order rate law 13. The kinetic data are collected in Tables III[25] and IV.

$$d[[LCuI]_2O]/dt = k_{13}[[LCuI]_2][O_2] \qquad (13)$$

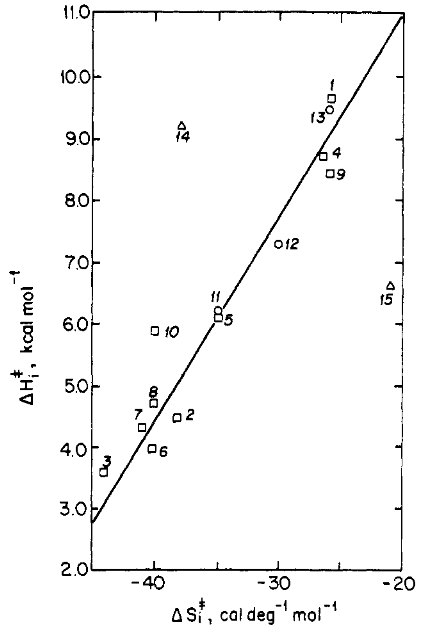


Figure 6. Plot of the activation enthalpy $\Delta H_i^{\ddagger}$ vs the corresponding activation entropy $\Delta S_i^{\ddagger}$ for second-order oxidations of excesses of the following complexes with dioxygen in nitrobenzene: $(py)_3Cu_3Co(NS)_2Cl_4$, 1: $(py)_3Cu_3Ni(NS)Cl_4$, 2; $(py)_3Cu_3Co(NS)Cl_4$, 3; $(py)_3Cu_3Zn(NS)Cl_4$, 4; $(py)_3Cu_3Cu(NS)Cl_4$, 5; $[NCuCl]_4$, 6; $N_3Cu_3Co(NS)Cl_4$, 7; $N_3Cu_3Ni(NS)Cl_4$, 8; $N_3Cu_3Zn(NS)Cl_4$, 9; $[NCuBr]_4$, 10; $[(TPED)CuI]_2$, 11; $[(TMPED)CuI]_2$, 12; $[(TMED)CuI]_2$, 13; $[NCuI]_4Y$, 14; $[NCuBr]_4Y$, 15. Typical errors for $\Delta H_i^{\ddagger}$ and $\Delta S_i^{\ddagger}$ are ±0.5 kcal mol^{-1} and ±4 cal deg^{-1} mol^{-1}, respectively. The data are taken from refs 2g, 5a, 11, 14, and 15, and the rate laws being compared are eqs 2, 9, and 13 (see also footnote 13). Ligands N and py are *N*,*N*-diethylnicotinamide and pyridine, respectively, NS is monoanionic *S*-methyl isopropylidenehydrazinecarbodithioate (see refs 14 and 15), and Y is 3,4,5,6-tetrachlorocatecholate (see ref 20). A very good correlation is observed except for points 14 and 15 (see text).

Interpretation of the Kinetic Data. Perhaps the most important finding of this work is that changing the halide from chloride or bromide to iodide in $[LCuX]_2$–dioxygen reactions results in a change from a third-order rate law (eq 4)[5b–d] to a second-order rate law (eq 13). This signals a change in the rate-determining step for copper(I) oxidation. An idea of how this happens can be gotten by comparing the data for second-order rate laws 2, 9, and 13.

Reactions 1 are governed by second-order rate law 2 with rate constants k_T.[5a,11] When X is Cl, they characteristically have $\Delta H_T^{\ddagger}$ = 2.1–4.2 kcal mol^{-1} and very negative $\Delta S_T^{\ddagger}$ = −(35–58) cal deg^{-1} mol^{-1}. Changing X to Br results in decreased rates because $\Delta H^{\ddagger}$ increases by 2–4 kcal mol^{-1} with the same order of magnitude for $\Delta S_T^{\ddagger}$. These and other data[14,15] indicate dioxygen insertion into

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(25) Supplementary material.

the halide cores of the reductants as the rate-determining step of reactions 1.[5a,11,13-15]

When X = Br, 10^2k_T for reaction 1 with N = *N,N*-diethylnicotinamide is 58 M^{-1} s^{-1} at 25 °C in nitrobenzene.[5a] Rate constant k_9 for the oxidation of $[NCuI]_4Y$ in reaction 8 is lower by a factor of ca. 5.[20] The proposed core structure of $[NCuI]_4Y$ (Scheme I) contains bridging catecholate on one face that would seriously impede O_2 insertion through that face. Since the products of reactions 8 are mono(μ-oxo)copper(II) complexes, insertion of O_2 through the halide cores of $[NCuX]_4Y$ is unnecessary for their formation.[20] In line with this reasoning, we find that the data for rate law 9 and the corresponding data for second-order oxidation of $[NCuBr]_4Y$ by dioxygen[20] do not fit the linear activation parameter correlation in Figure 6.

It has been proposed that reactions 9 proceed via the alternative mechanism shown in Scheme I.[20] Assumption of a steady state for respective intermediates II (X = Br, I) gives eqs 14 and 15.

$$[\mathrm{II}] = k_{14}[[NCuX]_4Y][O_2]/(k_{-14} + k_{15}[[NCuX]_4Y]) \quad (14)$$

$$d[[NCuX]_4Y(O)]/dt = 2k_{15}[[NCuX]_4Y][\mathrm{II}] = 2k_{14}k_{15}[[NCuX]_4Y]^2[O_2]/(k_{-14} + k_{15}[[NCuX]_4Y]) \quad (15)$$

Equation 15 has two obvious limits. One limit, $k_{-14} \ll k_{15}[[NCuX]_4Y]$, gives eq 16, which has the same second-order form as rate law 9, with $k_9 = 2k_{14}$. This situation corresponds

$$d[[NCuX]_4Y(O)]/dt = 2k_{14}[[NCuX]_4Y][O_2] \quad (16)$$

to rate-determining formation of "peroxocopper" intermediate II and its much faster reduction by a second mole of $[NCuX]_4Y$.[20] It is a reasonable conclusion because the copper(I) centers of $[NCuX]_4Y$ should be especially stabilized by X = Br and I.[19]

Assumption of a similar limiting mechanism for the oxidation of $[LCuI]_2$ complexes by dioxygen in nitrobenzene leads to the same conclusion: the rate-determining step is the reversible oxidation of one molecule of $[LCuI]_2$ by one molecule of O_2 to give some sort of "peroxocopper(II)" intermediate $[LCuI]_2(O_2)$. This is again a reasonable conclusion because copper(I) is especially stabilized by iodide.[19] We imagine that $[LCuI]_2(O_2)$ has the same sort of "peroxide" geometry as that shown in Scheme I because of the known[7] short Cu⋯Cu separations in $[LCuI]_2$. In any event, this intermediate is rapidly reduced by excess $[LCuI]_2$.[26]

The question now is why the kinetic data for rate law 13 fit the very good correlation of activation parameters for insertion-limited[2g,5a,11,14,15] copper(I) oxidation reactions in Figure 6. Is it possible that oxidations of $[LCuI]_2$ by O_2 require slow insertion of the dioxygen molecule through the planar[7,12] face Cu(I,I)Cu between the copper(I) centers? Lower second-order rate constant k_{13} on changing L from TEED to TMED (Table IV) could be due to a decrease in the Cu⋯Cu separation from 2.66 to 2.58 Å in the respective reductants $[LCuI]_2$.[7] A decrease in the width of the $[LCuI]_2$ core would slow down a penetration reaction. In any event, the negative activation entropies for rate law 13 (Table IV) indicate an associative slow step for $[LCuI]_2$ oxidation by dioxygen.

Acknowledgment. This work was supported by Grants INT-8715384, INT-8918985, and CHE-8717556 from the National Science Foundation, which are gratefully acknowledged. We thank Drs. Arthur Heiss and Ralph Weber of Bruker Instruments for help with the EPR measurements and Noralie Barnett and Amro El-Maradne for technical assistance.

Supplementary Material Available: Table III, giving kinetic data for the oxidation of dimeric iodocopper(I) complexes $[LCuI]_2$ by dioxygen in nitrobenzene (1 page). Ordering information is given on any current masthead page.

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(26) A reviewer suggested that the intermediates in $[LCuI]_2/O_2$ reactions could be hypoiodito complexes $[LCu(IO)]_2$ rather than peroxo complexes $[LCuI]_2O_2$. We know of no precedent for amine(hypoiodito)copper(II) complexes.

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Electron Spin Resonance Studies of "FeO_6" Tris Chelate Complexes: Models for the Effects of Zero-Field Splitting in Distorted $S = {}^5/_2$ Spin Systems

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Received May 12, 1988

The electron spin resonance (ESR) spectra of a series of substituted malonato and oxalato, high-spin, tris chelate complexes of iron(III) have been determined at both X- and Q-band frequencies for powdered polycrystalline samples in the temperature range 300–77 K. A diverse range of frequency-dependent spectra are reported, and these spectra are interpreted by using a spectrum simulation program based on matrix diagonalization methods for a general spin Hamiltonian incorporating electronic Zeeman and zero-field splitting terms. Data are presented that serve to form a library of spectra for octahedrally distorted $S = {}^5/_2$ spin systems. The observed spectra of these tris-chelate complexes vary with counterion, substituent on the ligand, and degree of hydration in an unpredictable manner.

Introduction

The $\{Fe^{III}O_6\}$ moiety in coordination complexes may be used as an active-site model[2] for some aspects of iron(III) chemistry in certain biological systems as well as an example of inherent photochemical reactivity.[3] Electron spin resonance (ESR) spectroscopy may be a sensitive probe of the metal site geometry in such circumstances. Photosensitive iron(III) complexes have been much used in imaging systems;[4] for example tris(oxalato)ferrate(III), $[Fe(ox)_3]^{3-}$, has been used in non-silver photographic printing processes such as the platinotype and blueprint methods. During the course of our investigations of the photoactivity of a range of dicarboxylato complexes of iron(III), we discovered that the details of the electronic structure, as assessed by ESR spectroscopy, of a seemingly closely related set of such complexes displayed an unexpected variety. A most sensitive spectroscopic probe of such systems comes from the application of multifre-

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