Inorganica Chimica Acta, *197* (1992) 197–201

Stoichiometry, properties and kinetics of aprotic reduction of dioxygen by $[LCuX]_2$ (L = *N,N*-diethylnipecotamide; X = Cl, Br)

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(Received March 2, 1992; revised May 4, 1992)

Abstract

This paper reports the synthesis of dimeric halocopper(I) complexes using *N,N*-diethylnipecotamide as a six-membered bidentate chelating ligand. Such dimeric copper(I) complexes react stoichiometrically with half dioxygen to form the stable oxocopper(II) derivatives, which can be converted to carbonatocopper(II) by CO_2. Spectra and kinetics of oxidation in aprotic media have been discussed.

Introduction

Metal-catalyzed reactions of O_2 play crucial parts in many biochemical and industrial processes [1, 2]. The copper(I)/copper(II) couple is an important catalyst for O_2 reactions [3] but its mechanisms of action are not as well understood as those of metals like iron and cobalt [4–6]. Many copper-catalyzed reactions are initiated by reaction of copper(I) with O_2 [2–4].

Karlin and co-workers have shown that biomimetic copper(I) dimers react with O_2 in aprotic solvents near −80 °C to give copper(II) complexes with different peroxo bridge geometries that can be distinguished chemically [4, 5]. Kinetic studies of peroxo complex formation, dissociation and intramolecular oxygenase transformation have been reported [6]. Peroxocopper complexes that simulate the functions of copper metalloenzymes like hemocyanins and tyrosinases under ambient conditions are actively being sought [5].

Simple copper–ligand catalysts have been focussed on because of their industrial importance [7]. Although copper(I) complexes exhibit a wide range of structures in the solid state [8, 9], simple halide-bridged molecules like $(py,DENC)_4Cu_4X_4$ and $N_2Cu_2X_2$ self-assemble in weakly coordinating solvents like methylene chloride when X is Cl, Br or I, the ligand is monodentate pyridine (py) or *N,N*-diethylnicotinamide (DENC) and N is a bidentate *N,N,N,N*-tetraalkyldiamine.

A strong thermodynamic driving force for ambient oxidation of these polynuclear copper(I) complexes to oxocopper(II) products by O_2 results in rate laws that reflect the copper reductant nuclearity (dimer or tetramer) when X is Cl or Br [8–13].

Peroxo and oxocopper(II) complexes contain basic oxygen sites that can deprotonate substrates [4, 6, 11, 14, 15] and initiate useful copper-catalyzed reactions [8, 9].

The objective of this work is to compare the *N,N*-diethylnipecotamide with the fully alkylated diamine from the formation and stability of the corresponding oxocopper(II) products.

Experimental

Materials

N,N-Diethylnipecotamide (L, Aldrich) was distilled under reduced pressure immediately before use. Copper(I) halides, CuX (X = Cl, Br), were prepared by the literature method [16] 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 [11]. High purity dinitrogen was deoxygenated by passage through a column of Alfa DE-OX solid catalyst.

Synthesis of reactants $[LCuX]_2$ (X = Cl, Br)

Solutions of L (2.50 mmol) in methylene chloride (30 ml) under dinitrogen were treated with 2.50 mmol of copper(I) chloride and copper(I) bromide, respectively, at room temperature. The mixtures were stirred under dinitrogen until clear solutions were obtained. Solid samples of $[LCuX]_2$ (X = Cl, Br) were obtained by vacuum solvent evaporation at room temperature and stored under dinitrogen. Analytical and cryoscopic

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molecular weight data are given in Table 1. Molecular weights, M_r, were determined by cryoscopy in nitrobenzene (m.p. 5.70 °C, $k_f = 7.00$ C molal) [17].

Dioxygen uptake measurements

The consumption of dioxygen by nitrobenzene solutions of $[LCuX]_2$ from the previous section was monitored by standard Warburg manometry [17] at room temperature. Reaction stoichiometry $\Delta[Cu(I)]/\Delta[O_2] = 4.0 \pm 0.1$ was generally completed in less than 6 h.

Oxidation products

The products of oxidation of methylene chloride solutions of $[LCuX]_2$ (X = Cl, Br) by dioxygen in the absence and presence of excess carbon dioxide were isolated as solids by solvent evaporation after gel permeation chromatography on Biobeads SX-12 resin with methylene chloride as the eluent. Analytical and cryoscopic data for the respective neutral dimeric products $[LCuX]_2O$ and $[LCuX]_2CO_3$ (X = Cl, Br) are collected in Table 1.

Physical measurements

IR spectra, in KBr disks or in solution, were obtained on a Perkin-Elmer model 567 spectrophotometer calibrated with the 906.5 or 3026.3 cm^{-1} absorptions of polystyrene. The electronic spectra were measured with a Beckman DB-G spectrophotometer in matched quartz cells at room temperature. EPR spectra of 1.0 mM solutions of these complexes in methylene chloride were measured with a Varian E-9 instrument.

Kinetic measurements of oxidation reactions were made by monitoring absorbance increase as a function of time at fixed wavelength in the region 600–700 nm with a computer-assisted stopped-flow spectrophotometer [18], which has an all glass-quartz flow system and is interfaced with a Digital Equipment PRO-350 computer. All kinetic measurements were conducted with a sufficient excess of reductants $[LCuX]_2$ (X = Cl, Br) to ensure a pseudo-first-order system. The total reactant concentration range was $[LCuX]_2 = (7.04\text{–}14.14) \times 10^{-3}$ M, with $[O_2]_0 = 4.4 \times 10^{-4}$ M. Temperature was controlled to ±0.05 °C in the range 20.0–45.0 °C.

TABLE 1. Analytical and cryoscopic data for $[LCuX]_2$, $[LCuX]_2O$ and $[LCuX]_2CO_3$ complexes (X = Cl, Br)

Complex	Anal. (%)[a]					M_r[b]
	C	H	N	X	Cu	
$[LCuCl]_2$[c]				12.82	22.77	540
				(12.54)	(22.44)	(566)
$[LCuBr]_2$[c]				24.63	20.00	620
				(24.43)	(19.39)	(655)
$[LCuCl]_2O$	41.41	6.92	9.59	12.57	22.18	568
	(41.24)	(6.87)	(9.62)	(12.20)	(21.82)	(582)
$[LCuBr]_2O$	35.91	6.02	8.25	24.01	18.90	640
	(35.77)	(5.96)	(8.35)	(23.85)	(18.93)	(671)
$[LCuCl]_2CO_3$	40.42	6.61	9.02	12.44	19.91	600
	(40.26)	(6.39)	(8.95)	(11.34)	(20.29)	(626)
$[LCuBr]_2CO_3$	36.00	5.72	8.01	22.70	17.42	680
	(35.24)	(5.59)	(7.83)	(22.38)	(17.76)	(715)

[a] Calculated values in parentheses. [b] Measured in nitrobenzene at the $(3\text{–}5) \times 10^{-2}$ molal level. [c] Immediately analyzed for X and Cu after sample preparation.

Results and discussion

Copper(I) halides react quantitatively with *N,N*-diethylnipecotamide (L) in oxygen-free, weakly coordinating aprotic solvents such as methylene chloride or nitrobenzene to form dimeric complexes $[LCuX]_2$, where X = Cl, Br, eqn. (1). Cryoscopic determination establishes the formation of discrete dimeric products $[LCuX]_2$, Table 1.

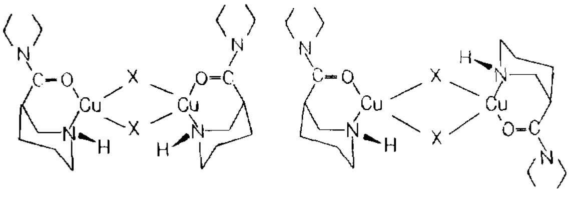
$$2L + 2CuX \longrightarrow [LCuX]_2 \qquad (1)$$

IR spectra of free L and [LCuX]₂

Major features of the KBr disk IR spectra show a change in ν(NH) from 3500 cm^{-1} for the free ligand to 3420 cm^{-1} for $[LCuX]_2$, X = Cl or Br. The 1625 cm^{-1} absorption assigned to amide carbonyl for the free ligand is converted to a split band centered at 1625 and 1570 cm^{-1} in $[LCuX]_2$ [19]. Such changes in IR confirm that the ligand L coordinated to the copper(I) center by the pyrrole NH and the amide carbonyl to form a six-membered chelating ring with copper(I). The dimeric $[LCuX]_2$ can exist as either the *cis* or *trans* isomer (Scheme 1).

Reaction of copper(I) complexes with dioxygen

Measurements of dioxygen uptake were consistent with a reaction stoichiometry given by eqn. (2), where X = Cl, Br. This stoichiometry, $\Delta[Cu(I)]/\Delta[O_2] = 4.0$, is expected in systems involving a complete reduction of dioxygen to oxo and non-oxidizable ligands [20]. Cryoscopic and analytical data for the reaction products are listed in Table 1. The cryoscopic data indicate that $[LCuX]_2O$ complexes like their copper(I) precursors,



Scheme 1. *cis* and *trans* isomers of $[LCuX]_2$ where L = *N,N*-diethylnipecotamide.

TABLE 2. EPR and electronic spectral data for $[LCuX]_2O$ and $[LCuX]_2CO_3$ complexes (X = Cl, Br) in methylene chloride

Complex	Temperature (K)	$A_{\parallel}$[a]	EPR				λ_{max} (nm) (ϵ_λ ($M^{-1}cm^{-1}$))
			$g_{\parallel}$	$g_{\perp}$	g ($\Delta M_s=2$)	g_i	
$[LCuCl]_2O$	300					2.11	750(199); 825(190)
	25	80	2.22	2.10	4.16		
$[LCuCl]_2CO_3$	300					2.12	750(192); 825(182)
	25	90	2.22	2.11	4.19		
$[LCuBr]_2O$	300					2.12	750(134); 825(119)
	25	110	2.22	2.06	4.19		
$[LCuBr]_2CO_3$	300					2.12	750(167); 825(159)
	25	120	2.24	2.09	4.22		

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

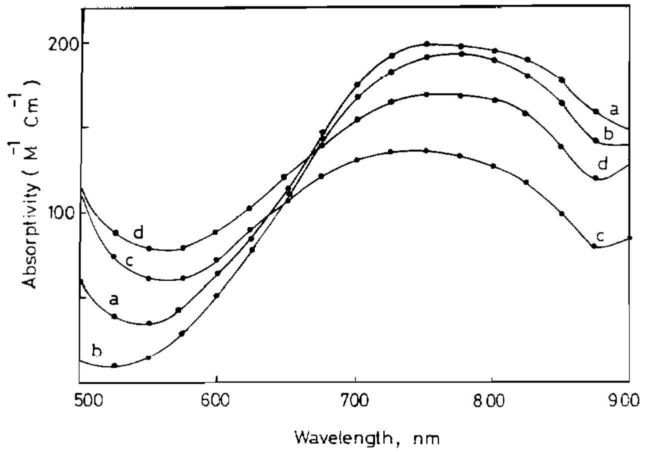


Fig. 1. Electronic spectra of $[LCuCl]_2O$ (a), $[LCuCl]_2CO_3$ (b), $[LCuBr]_2O$ (c) and $[LCuBr]_2CO_3$ (d) in methylene chloride at 25 °C.

are discrete dinuclear species which have no tendency to disproportionate or polymerize as found in oxocopper(II) species with alkylated diamine ligands [21].

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

Carbonatocopper(II) derivatives

They can be formed either by oxidation of dimeric copper(I), $[LCuX]_2$, with dioxygen in the presence of CO_2 gas or by bubbling CO_2 through an oxo solution, $[LCuX]_2O$, eqns. (3a) and (3b). Cryoscopic and analytical data, Table 1, establish the formation of $[LCuX]_2CO_3$ (X = Cl, Br). Attempted crystallization of oxo or carbonatocopper(II) derivatives with different procedures failed to produce single crystals of $[LCuX]_2O$ or $[LCuX]_2CO_3$.

$$2[LCuX]_2 \xrightarrow{O_2/2CO_2} 2[LCuX]_2CO_3 \qquad (3a)$$

$$[LCuX]_2O \xrightarrow{CO_2} [LCuX]_2CO_3 \qquad (3b)$$

IR and electronic spectra

The IR spectra of $[LCuX]_2O$ and $[LCuX]_2CO_3$ show the same behaviour for pyrrole NH and amide carbonyl as in $[LCuX]_2$, suggesting a six-membered chelating ring for L through pyrrole NH and amide carbonyl.

The room-temperature electronic spectra of oxo and carbonatocopper(II) derivatives in methylene chloride exhibit broad maxima around 750 nm with a shoulder centered at about 825 nm. Representative data are shown in Table 2 and Fig. 1. The spectral ranges of these ligand field bands are characteristic of distorted five-coordinate copper(II) complexes [12, 22].

EPR spectra

The X-band EPR spectra of $[LCuX]_2O$ and $[LCuX]_2CO_3$, Table 2, indicate axial-type structures with $g_{\parallel} > g_{\perp}$ in agreement with a $d_{x^2-y^2}$ ground state for a distorted square-pyramidal configuration. All the complexes exhibit a single triplet transition ($\Delta M_s = 2$) due to the interaction between the two copper centers in the dimeric complexes [21].

The kinetics of oxidation of $[LCuX]_2$ complexes by dioxygen in nitrobenzene

The reactions are easily monitored spectrophotometrically in the visible region (650–850 nm) and the rates fall in the stopped-flow time domain.

First-order plots of log $(A_\infty - A_t)$ versus time, where A_t is the absorbance of $[LCuX]_2O$ (X = Cl, Br) at time t, were linear for at least four half-lives, Fig. 2, indicating that reaction (eqn. (2)) is first order in $[O_2]$. Absorbances extrapolated to zero time correspond to those expected for the copper(I) reactant at monitoring wavelength, thus providing no evidence for reactant preequilibria. The simple first-order rate dependence indicates either that significant concentrations of reaction intermediates are not formed or that they do not absorb appreciably in the monitoring wavelength. The derived pseudo-first-order rate constants, K_{obs}, were accurately proportional to $[[LCuX]_2]^2$ at fixed temperature to give straight lines

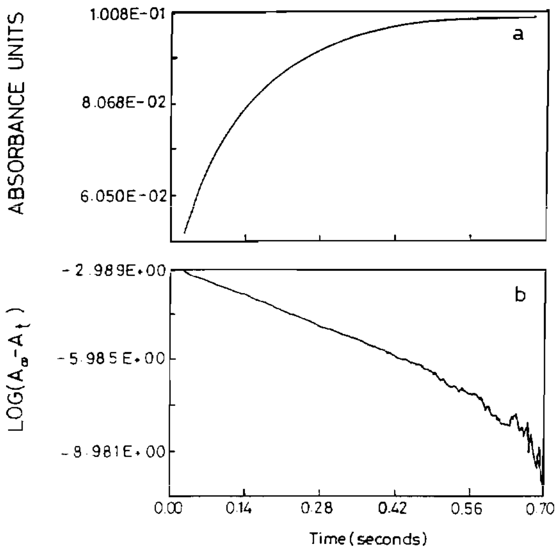


Fig. 2. (a) Absorbance–time data for the reaction of $[LCuBr]_2$ (14.08 mM) with dioxygen (0.44 mM) in nitrobenzene at 22.9 °C. Monitoring wavelength is 650 nm. (b) Computer-generated plot of log $(A_\infty - A_t)$ vs. time for the data in the upper panel.

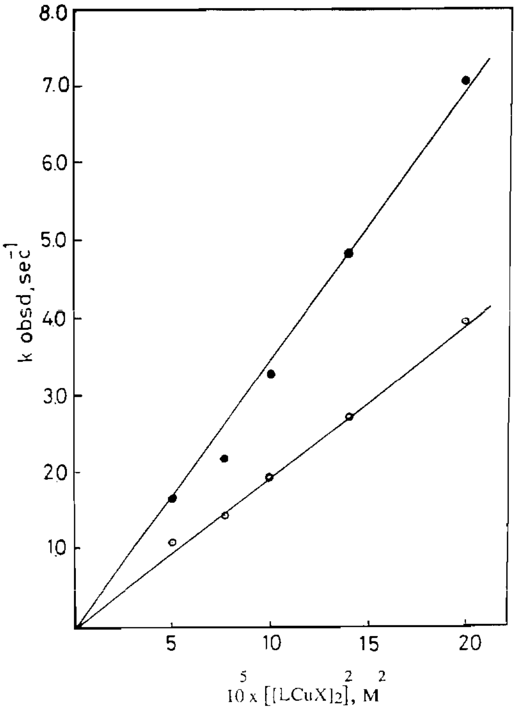


Fig. 3. Dependence of the observed pseudo-first-order rate constant k_{obs} vs. $[[LCuX]_2]^2$ where X = Cl(○) and Br(●) in nitrobenzene at 25.2 °C for Cl and 22.9 °C for Br.

passing through the origin, Fig. 3. This indicates irreversible reaction with a third-order process, eqn. (4), when $[LCuX]_2$ is in excess. Third-order rate constants k_D and their associated activation parameters are listed in Table 3.

TABLE 3. Kinetic parameters for oxidation of $[LCuX]_2$ (X = Cl, Br) by dioxygen in nitrobenzene

Reductant	Temperature (°C)	k_D[a]	$\Delta H^\ddagger_D$[b]	$\Delta S^\ddagger_D$[c]
$[LCuCl]_2$	25.20	21800		
	27.60	22400		
	31.60	25000		
	43.80	32000	4.1	−25
$[LCuBr]_2$	22.90	33000		
	25.00	35000		
	31.80	44800		
	37.60	52000		
	42.50	60200	5.4	−20

[a] Units are $M^{-2}\ s^{-1}$; typical error is ±5%. [b] Units are K cal mol^{-1}; typical error is ±0.4 K cal mol^{-1}. [c] Units are cal $deg^{-1}\ mol^{-1}$ at 25 °C; typical error is ±3 cal $deg^{-1}\ mol^{-1}$.

$$-\frac{d[O_2]}{dt} = k_D[[LCuX]_2]^2[O_2] \tag{4}$$

Features of the kinetic data

The major features of the kinetic data for $[LCuX]_2$ oxidation by dioxygen in aprotic solvents are as follows.

(i) Small activation enthalpies are found in the oxidation of $[LCuX]_2$ (X = Cl, Br) indicating little necessity for structural rearrangements on activation of the reactants. Negative activation entropies indicate substantial associative character in the activation process.

(ii) Changing X = Cl to X = Br always causes $\Delta H^\ddagger_D$ and $\Delta S^\ddagger_D$ to increase in (N) ligand and alkylated diamine [12, 23]. However k_D in L ligand does not change much.

(iii) On comparing the activation parameters of $[LCuX]_2$ oxidation with the diamine systems [12], L was found to be similar to the less steric diamine, tetramethylethylenediamine (TMED).

(iv) $\Delta H^\ddagger_D$ and $\Delta S^\ddagger_D$ for $[LCuX]_2$ (X = Cl, Br) lie on the linear plot of $\Delta H^\ddagger_D$ versus $\Delta S^\ddagger_D$ for all diamine ligands [12], suggesting similar activation requirements.

Interpretation of the kinetic data

Oxidation of $[LCuX]_2$ proceeds as shown in eqns. (5)–(8).

$$[LCuX]_2 + O_2 \underset{K_{-1}}{\overset{K_1}{\rightleftharpoons}} [LCuX]_2O_2 \tag{5}$$

$$[LCuX]_2O_2 + [LCuX]_2 \xrightarrow[\text{slow}]{k_2} [[LCuX]_2]_2O_2 \tag{6}$$

$$[[LCuX]_2]_2O_2 \xrightarrow{\text{fast}} 2[LCuX]_2O \tag{7}$$

$$-\frac{d[O_2]}{dt} = k_2[[LCuX]_2O_2][[LCuX]_2] \tag{8}$$

Assumption of a steady-state concentration for the intermediate $[LCuX]_2O_2$ gives eqns. (9) and (10).

$$[[LCuX]_2O_2]=\frac{K_1[[LCuX]_2][O_2]}{K_{-1}+k_2[[LCuX]_2]} \tag{9}$$

$$\frac{-d[O_2]}{dt}=\frac{k_2K_1[[LCuX]_2]^2[O_2]}{K_{-1}+k_2[[LCuX]_2]} \tag{10}$$

Under the experimental conditions, there is no indication for any equilibrium. Such a result means that $k_{-1} \gg k_2[[LCuX]_2]$ to give eqn. (11).

$$\frac{-d[O_2]}{dt}=Kk_2[[LCuX]_2]^2[O_2] \tag{11}$$

Equations (4) and (11) have the same third-order form, with $k_D=Kk_2$, and correspond to rate-determining reduction of the intermediate complex $[LCuX]_2O_2$ by excess $[LCuX]_2$. Assembly of the appropriate activated complex is confirmed by the fit of the $\Delta H_D^\ddagger$ versus $\Delta S_D^\ddagger$ relation of these data with diamine data [12].

Conclusions

The stable oxo complexes $[LCuX]_2O$ show a much higher stability than the alkylated diamine ligands such as $[(TMED)CuX]_2O$. Such stability could be due to hydrogen bonding between the pyrrole hydrogen and the oxo group. The clarity of the kinetic reactions indicate that copper(I) complexes $[LCuX]_2$ (X = Cl, Br) either exist in one isomeric form or in *cis–trans* forms of $[LCuX]_2$ which are oxidized at the same rate (Scheme 1).

Acknowledgements

This work was supported by Grants from the United Arab Emirates University and INT-8715384 from the National Science Foundation. I thank Professor Geoffrey Davies for valuable discussions and Professor William Orme-Johnson for help with EPR measurements.

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