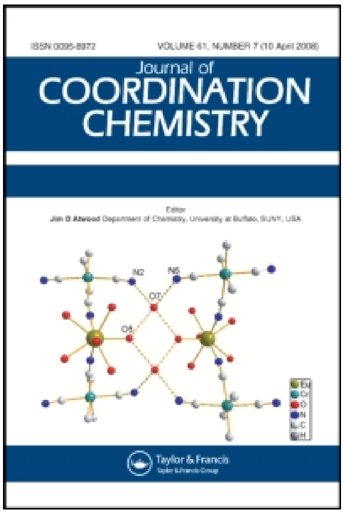

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Homogeneous oxidative coupling catalysts: stoichiometry, characterization and kinetics of [(diamine)(μ-halo)copper(I)]$_2$ oxidation by dioxygen in aprotic solvent

Mohamed A. El-Sayed[a]; Ibrahim A. Abdel-Hamid[a]; Tahani A. El-Zayat[a]; Ahmed H. Abdel Salam[a]; Hisham A. Abo El-dahab[a]
[a] Faculty of Science, Chemistry Department, Alexandria, Egypt

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Homogeneous oxidative coupling catalysts: stoichiometry, characterization and kinetics of [(diamine)(μ-halo)copper(I)]$_2$ oxidation by dioxygen in aprotic solvent

MOHAMED A. EL-SAYED†*, IBRAHIM A. ABDEL-HAMID,
TAHANI A. EL-ZAYAT, AHMED H. ABDEL SALAM and
HISHAM A. ABO EL-DAHAB

Faculty of Science, Chemistry Department, P.O. 426, El-Ibrahimeia 21321,
Alexandria, Egypt

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Copper(I) halides dissolve in deoxygenated methylene chloride and nitrobenzene solutions of equimolar *N*,*N*,*N*′-triethylethylenediamine (TriEED) to give air-sensitive colorless or pale yellow copper(I) dimers [(TriEED)(μ-X)Cu]$_2$, X = Cl, Br or I. Dioxygen uptake, analytical, cryoscopic and spectral data show that copper(I) dimers are oxidized to μ-oxo complexes, [(TriEED)$_2$(μ-X)$_2$(μ-O)Cu$_2$], which react with carbon dioxide to form μ-carbonato analogues, [(TriEED)$_2$X$_2$(μ-CO$_3$)Cu$_2$]. Both oxo and carbonato complexes are homogeneous oxidative coupling catalysts for oxidation of 2,6-dimethylphenol to mixture of diphenoquinone (DPQ) and polyphenyleneoxide (PPO). Kinetic data for oxidation of [(TriEED)(μ-X)Cu]$_2$ by dioxygen in nitrobenzene obey the third-order rate law $d[[(TriEED)_2(\mu\text{-}X)_2(\mu\text{-}O)Cu_2]]/dt = k_D[[(TriEED)(\mu\text{-}X)Cu]_2]^2[O_2]$. Comparison of the kinetic data with data for oxidation of [(TEED)(μ-Br)Cu]$_2$, TEED = *N*,*N*,*N*′,*N*′-tetraethylethylenediamine (the fully alkylated diamine), by dioxygen indicate that N–H in (TriEED) speeds the reaction by a factor of 220 due to an intermolecular attractive force between N–H of (TriEED) and the incoming dioxygen, helping to assemble the activated complex.

Keywords: Diamine copper(I) halides; Dioxygen reactions; 2,6-dimethylphenol oxidation

1. Introduction

Copper(I)/O$_2$ reactions play key roles in many Cu-catalyzed processes [1–6]. Copper(I) halides have a high affinity for polyamines. The diamine complexes are halo-bridged LCu(X, X)CuL dimers with Cu–Cu distance from 2.56 to 2.73 Å [7].

[(Diamine)(μ-halo)copper(I)]$_2$ complexes **D** (scheme 1) are homogeneous catalysts for important industrial reactions [8] with dioxygen in aprotic solvents.

The product of equation (1) is a neutral, green μ-oxo dimer **C** (scheme 1), L = *N*,*N*′-diethylethylenediamine, DEED [10]. equation (2) gives a neutral, blue tetranuclear

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*Corresponding author. Email: maelsayed_chem@yahoo.com

†Present address: Gazan University, Chemistry Department, Gazan, Saudi Arabia.

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mixed valence peroxo complex **A** (scheme 1) when L = TEED, X = Cl at temperatures less than −26°C [11] or L = DEED, X = Br for less than 3.2 h [10].

$$2\underset{\mathbf{D}}{[\mathrm{L}(\mu\text{-X})\mathrm{Cu}]_2} + \mathrm{O}_2 \longrightarrow 2\underset{\mathbf{C}}{[\mathrm{L}_2(\mu\text{-X})_2(\mu\text{-O})\mathrm{Cu}_2]} \qquad (1)$$

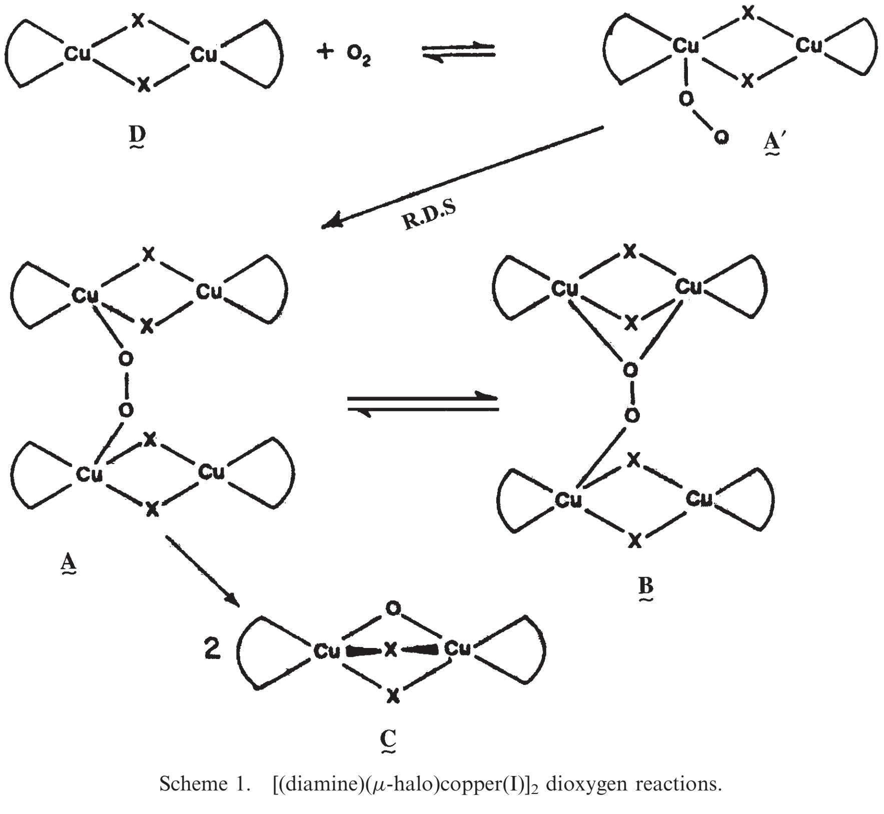
$$2\underset{\mathbf{D}}{[\mathrm{L}(\mu\text{-X})\mathrm{Cu}]_2} + \mathrm{O}_2 \longrightarrow \underset{\mathbf{A}}{[(\mu\text{-O}_2)[\mathrm{L}_2(\mu\text{-X})_2\mathrm{Cu(I)Cu(II)}]_2]} \qquad (2)$$

Oxidation of $[\mathrm{L}(\mu\text{-X})\mathrm{Cu}]_2$, L = tetraalkyldiamine, X = Cl, Br, are third-order, equation (3) [9]; the slowest step in equation (1) is assembly of the activated complex from two dimers and one O_2 [9].

$$d[[\mathrm{L}_2(\mu\text{-X})_2(\mu\text{-O})\mathrm{Cu}_2]]/dt = k_\mathrm{D}[\mathrm{O}_2][[\mathrm{L}(\mu\text{-X})\mathrm{Cu}]_2]^2 \qquad (3)$$

The transfer of four electrons from Cu(I) centers to O_2 is fast at ambient temperatures and no intermediate oxidation states have been detected.

Oxidation of $[\mathrm{L}(\mu\text{-X})\mathrm{Cu}]_2$, L = TEED, X = CL at low temperature (less than −26°C) and L = DEED, X = Br at temperature from −51°C, temperature to 30°C are also third-order [10, 11], proceeding via identifiable peroxo complexes, $[(\mu\text{-O}_2)[\mathrm{L}_2(\mu\text{-X})_2\mathrm{Cu(I)Cu(II)}]_2]$ **A** (scheme 1). The third-order rate constants have 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.



Scheme 1. [(diamine)(μ-halo)copper(I)]$_2$ dioxygen reactions.

Peroxo complexes **A** and **B** exist in slow equilibrium from −78 to −50°C for TEED and −51 to −17°C for DEED. Conversion of **A** to **B** is exothermic and **A** dominates at higher temperatures. However, **A** is irreversibly converted to **C** with a half-life of 25 s at −35°C for TEED and a half-life of 3.2 h at 25°C for DEED.

The resistance of **A** to intramolecular Cu(I) → peroxo electron transfer with L = DEED and X = Br was attributed to hydrogen bonding between the N–H groups of DEED and bound peroxide and stabilization of Cu(I) by Br.

The objective of this work can be summarized in the following points: (a) what effect will TriEED with only one free NH have on oxidation? (b) studying the stoichiometry and characterizing the oxidized products. (c) examining reactivity of the oxidized products with carbon dioxide to form the carbonato analogue. (d) studying the kinetics of oxidation of $[L(\mu\text{-}X)Cu]_2$ by O_2 in nitrobenzene. (e) examining catalysis of the oxo and carbonato products in phenolic oxidative coupling?

2. Experimental

2.1. *Materials*

Triethylethylenediamine, TriEED, (Aldrich) were used as received. Copper(I) halides were prepared as described in the literature [12].

Nitrobenzene was distilled under reduced pressure from phosphorous pentaoxide and stored over 4 Å molecular sieves. Methylene chloride was washed with concentrated sulfuric acid, dried over anhydrous sodium carbonate, refluxed over phosphorous pentoxide, then distilled and stored over anhydrous sodium carbonate [13].

High purity dinitrogen gas was deoxygenated by passing through a column of Alfa DE-OX solid catalyst, and dried by passage through a 60-cm column of dehydrated silica gel and a 30-cm column of calcium chloride and molecular sieves.

2.2. *Synthesis of $[(TriEED)(\mu\text{-}X)Cu]_2$, $[(TriEED)_2(\mu\text{-}X)_2(\mu\text{-}O)Cu_2]$ and $[(TriEED)_2X_2(\mu\text{-}CO_3)Cu_2]$ (X = Cl, Br or I)*

A solution of TriEED (2.5 mmol) was dissolved in anhydrous methylene chloride under dinitrogen at 25°C. The appropriate copper(I) halide, CuX (2.5 mmol), was then added and the reaction mixture was stirred with a stream of dinitrogen until the solid dissolved, giving a colorless solution for X = Cl and Br and a pale yellow solution for X = I.

Treatment of $[(TriEED)(\mu\text{-}X)Cu]_2$ in methylene chloride at 25°C with excess dioxygen resulted in rapid formation of a deep green solution. The solvent was removed in a vacuum rotary evaporator, leaving a green solid of dimeric oxocopper(II) product, $[(TriEED)_2(\mu\text{-}X)_2(\mu\text{-}O)Cu_2]$; X = Cl, Br or I.

Treatment of $[(TriEED)(\mu\text{-}X)Cu]_2$ in methylene chloride at 25°C with excess carbon dioxide and dioxygen resulted in rapid formation of a deep green solution. The solvent was removed on a vacuum rotary evaporator, leaving a green solid of μ-carbonato dicopper(II) dimers, $[(TriEED)_2X_2(\mu\text{-}CO_3)Cu_2]$; X = Cl, Br or I.

Complexes were identified by cryoscopic molecular weight determination in nitrobenzene [11] using a Eutechnics Precision Temperature, model 4600 thermometer.

Elemental copper and halogen (Cl, Br) contents in each sample were determined as described in the literature [14, 15]. Carbon, hydrogen and nitrogen contents of $[(\mathrm{TriEED})_2(\mu\text{-X})_2(\mu\text{-O})\mathrm{Cu}_2]$ and $[(\mathrm{TriEED})_2\mathrm{X}_2(\mu\text{-CO}_3)\mathrm{Cu}_2]$ (X = Cl, Br or I) were determined at the Microanalytical Laboratory, Chemistry Department, Cairo University. Molecular weights and analytical data are collected in table 1.

2.3. *Physical measurements*

Electronic spectra for products in methylene chloride were measured with a Shimadzu Model 160A ultraviolet-visible recording spectrophotometer, in matched quartz cells at room temperature.

Infrared spectra of KBr disks for solid products or KBr plates for liquid ligand were obtained with a PERKIN-ELMER 1430 Ratio Recording Infrared Spectrophotometer at room temperature. The 906.5 or 3026.3 cm^{-1} absorptions of polystyrene were used for calibration. Room temperature EPR spectra of solid $[(\mathrm{TriEED})_2(\mu\text{-X})_2(\mu\text{-O})\mathrm{Cu}_2]$ and $[(\mathrm{TriEED})_2\mathrm{X}_2(\mu\text{-CO}_3)\mathrm{Cu}_2]$ (X = Cl, Br or I) complexes were measured at the King Fahd University of Petroleum and Minerals on a Radiopan Varian spectrometer at 100.00 KHz and at different G modulation amplitudes with a rectangular TE 102 cavity and 100 KHz modulation field. Resonance conditions were found at ca 9.7 GHz (X-band) at room temperature. The field was calibrated with a powder of diphenylpicrylhydrazyl (DPPH; $g = 2.0037$) [16].

2.4. *Dioxygen uptake measurements*

Consumption of dioxygen by nitrobenzene solutions of $[(\mathrm{TriEED})(\mu\text{-X})\mathrm{Cu}]_2$, X = Cl, Br or I, was monitored by standard Warburg manometry [17] at room temperature and atmospheric pressure.

Table 1. Analytical and cryoscopic data for $[(\mathrm{TriEED})_2(\mu\text{-X})_2(\mu\text{-O})\mathrm{Cu}_2]$ and $[(\mathrm{TriEED})_2\mathrm{X}_2(\mu\text{-CO}_3)\mathrm{Cu}_2]$ (X = Cl, Br or I).

	Anal. (%)[a]					
Complex	C	H	N	X	Cu	$\mathrm{M}_\mathrm{r}^\mathrm{b}$
$[(\mathrm{TriEED})_2(\mu\text{-Cl})_2(\mu\text{-O})\mathrm{Cu}_2]$	37.9	8.0	11.4	13.9	25.6	506
	(38.2)	(8.0)	(11.2)	(13.7)	(24.5)	(502)
$[(\mathrm{TriEED})_2\mathrm{Cl}_2(\mu\text{-CO}_3)\mathrm{Cu}_2]$	37.0	7.1	10.2	13.5	23.7	549
	(37.4)	(7.4)	(10.2)	(13)	(23.3)	(546)
$[(\mathrm{TriEED})_2(\mu\text{-Br})_2(\mu\text{-O})\mathrm{Cu}_2]$	32.2	6.6	9.3	26.4	21.4	597
	(32.5)	(6.8)	(9.5)	(27.0)	(21.5)	(591)
$[(\mathrm{TriEED})_2\mathrm{Br}_2(\mu\text{-CO}_3)\mathrm{Cu}_2]$	32.1	6.0	8.5	25.2	20.4	625
	(32.1)	(6.3)	(8.8)	(25.2)	(20.0)	(635)
$[(\mathrm{TriEED})_2(\mu\text{-I})_2(\mu\text{-O})\mathrm{Cu}_2]$	28.3	5.9	8.2	*	18.0	673
	(28.0)	(5.9)	(8.2)		(18.5)	(685)
$[(\mathrm{TriEED})_2\mathrm{I}_2(\mu\text{-CO}_3)\mathrm{Cu}_2]$	28.3	5.3	7.7	*	17.7	732
	(28.0)	(5.5)	(7.7)		(17.4)	(729)

[a] Calculated values in parentheses.
[b] Measured in nitrobenzene.
*Mixed halogen.

2.5. *Test of catalytic activity*

Solutions of various $[(\text{TriEED})_2(\mu\text{-X})_2(\mu\text{-O})\text{Cu}_2]$ and $[(\text{TriEED})_2\text{X}_2(\mu\text{-CO}_3)\text{Cu}_2]$ $(\text{X} = \text{Cl, Br or I})$, complexes in methylene chloride were added to 100 fold excess of 2,6-dimethylphenol in methylene chloride. Dioxygen was then bubbled through each solution for 20 min.

2.6. *Kinetic measurements*

The pseudo-first order rates of the reaction of excess dinuclear copper(I) complexes, $[(2\text{–}18) \times 10^{-3}\ \text{M}]$, $[(\text{TriEED})(\mu\text{-X})\text{Cu}]_2$, where $\text{X} = \text{Br}$ or I, with deficient concentration of dioxygen $[(2.2\text{–}4.4) \times 10^{-3}\ \text{M}]$ were monitored spectrophotometrically at 700 nm for $\text{X} = \text{Br}$ and 720 nm for $\text{X} = \text{I}$. A Beckman DB-G spectrophotometer (connected to a BAS X-Y recorder, which provides pens with maximum speeds of $2000\ \text{mm}^{-1}\ \text{s}$ for the X-axis), and fitted with a cell housing maintained within ±0.1°C of the desired temperature. All reactants were thermostated for at least 20 min before fast injection of dioxygen. Each reaction was monitored at least four half-lives (≈94%) for consumption of dioxygen (figure 1).

3. Results and discussion

Copper(I) halides dissolve in deoxygenated methylene chloride and nitrobenzene solutions of equimolar *N*,*N*,*N*′-triethylethylenediamine to give air-sensitive colorless or pale yellow copper(I) dimers $[(\text{TriEED})(\mu\text{-X})\text{Cu}]_2$, $\text{X} = \text{Cl}$, Br or I. Cryoscopic measurements in nitrobenzene under dinitrogen (table 1) confirm that the products are dimers.

The geometry of $[(\text{TriEED})(\mu\text{-X})\text{Cu}]_2$, $\text{X} = \text{Cl}$, Br or I, could best be described as previously determined $[\text{TEED})(\mu\text{-X})\text{Cu}]_2$ [18], which is a *bis*-(μ-bromo)-bridged dimer with a Cu–Cu distance averaging 2.6 Å. Each copper(I) atom exhibits a distorted tetrahedral coordination environment.

3.1. *Stoichiometric reactions of dimeric copper(I), [(TriEED)(μ-X)Cu]₂, X = Cl, Br or I, with dioxygen and with carbon dioxide in the presence of dioxygen*

Dioxygen uptake measurements were consistent with a reaction stoichiometry given by equation (4),

$$2[(\text{TriEED})(\mu\text{-X})\text{Cu}]_2 + \text{O}_2 \rightarrow 2[(\text{TriEED})_2(\mu\text{-X})_2(\mu\text{-O})\text{Cu}_2] \tag{4}$$

which indicates complete dioxygen reduction by dimeric copper(I) to produce dimeric μ-oxo copper(II) products. Treatment of the oxo complexes with excess carbon dioxide gives the corresponding (μ-carbonato) dicopper(II) dimers [equation (5)].

$$[(\text{TriEED})_2(\mu\text{-X})_2(\mu\text{-O})\text{Cu}_2] \xrightarrow{\text{CO}_2} [(\text{TriEED})_2\text{X}_2(\mu\text{-CO}_3)\text{Cu}_2] \tag{5}$$

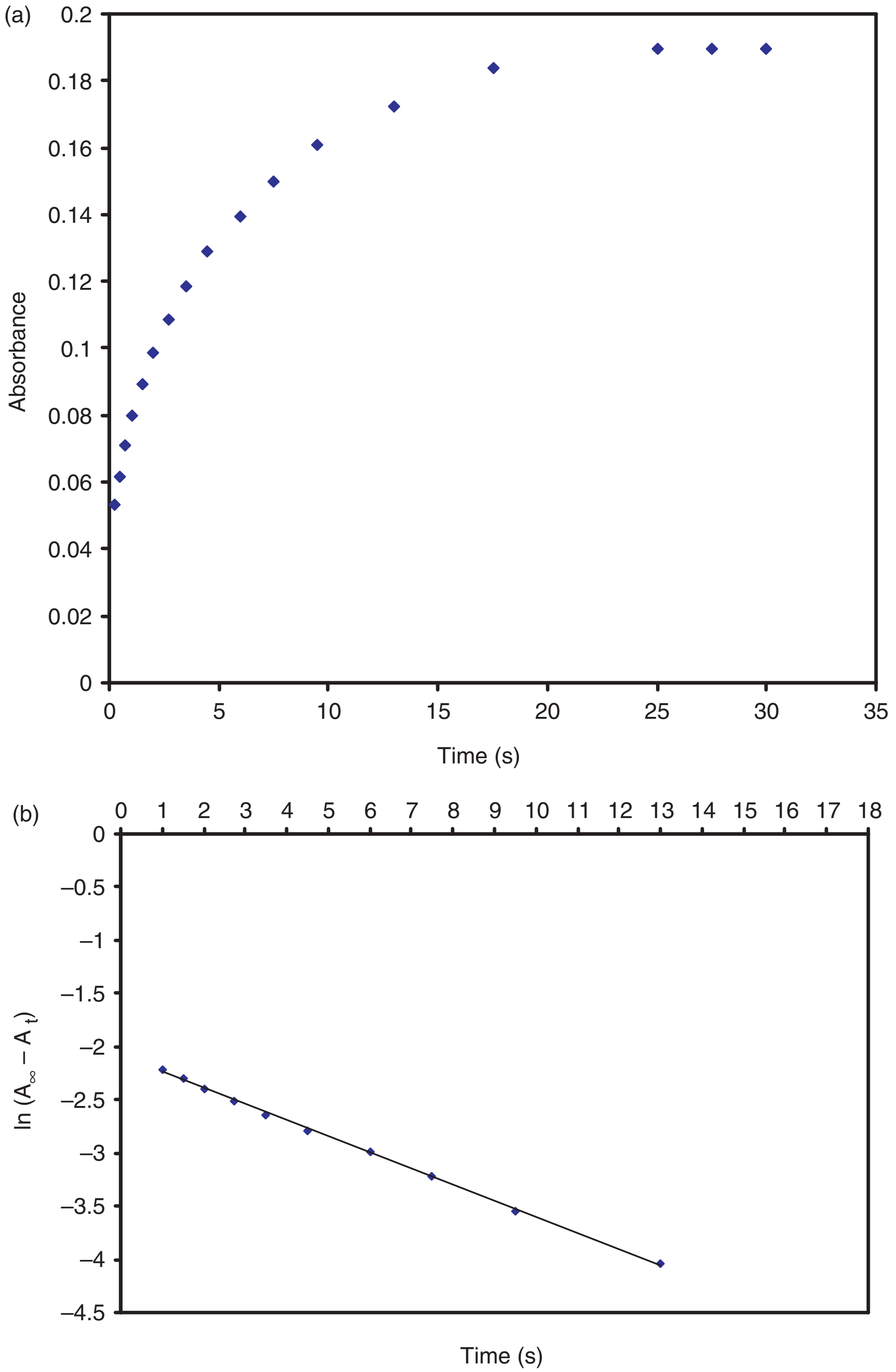


Figure 1. (a) Absorbance-time data for reaction of [(TriEED)(μ-I)Cu]$_2$ (4.9×10^{-3}M) with dioxygen (4.4×10^{-4} M) in nitrobenzene at 27°C. Monitoring wavelength is 720 nm. (b) first order plot of ln($A_\infty - A_t$) *vs*. time for the data in the upper panel.

Table 2. Room temperature solid-state X-band EPR and spectral data for $[(\text{TriEED})_2(\mu\text{-X})_2(\mu\text{-O})\text{Cu}_2]$ and $[(\text{TriEED})_2\text{X}_2(\mu\text{-CO}_3)\text{Cu}_2]$ (X = Cl, Br or I).

	EPR					
Complex	$A_{\parallel}^{a}$	$g_{\parallel}$	$g_{\perp}$	g_i	$g_{(\Delta Ms=\pm 2)}$	λ_{max}/nm (ε_{max}/M^{-1}cm^{-1})^b
$[(\text{TriEED})_2(\mu\text{-Cl})_2(\mu\text{-O})\text{Cu}_2]$	131	2.31	2.03	–	4.20	718(230)
$[(\text{TriEED})_2\text{Cl}_2(\mu\text{-CO}_3)\text{Cu}_2]$	121	2.32	2.04	–	4.20	718(260)
$[(\text{TriEED})_2(\mu\text{-Br})_2(\mu\text{-O})\text{Cu}_2]$	126	2.38	2.04	–	4.19	718(340)
$[(\text{TriEED})_2\text{Br}_2(\mu\text{-CO}_3)\text{Cu}_2]$	110	2.37	2.02	–	4.20	715(455)
$[(\text{TriEED})_2(\mu\text{-I})_2(\mu\text{-O})\text{Cu}_2]$	–	–	–	2.04	4.17	705(185)
$[(\text{TriEED})_2\text{I}_2(\mu\text{-CO}_3)\text{Cu}_2]$	–	–	–	2.07	4.19	700(330)

[a] Units are $10^{-4}\,\text{cm}^{-1}$.
[b] Measured in methylene chloride.

Carbonato complexes can also be formed when dimeric copper(I) complexes, $[(\text{TriEED})(\mu\text{-X})\text{Cu}]_2$, are oxidized by dioxygen in the presence of excess carbon dioxide.

The molecular structures of (μ-carbonato) dicopper(II) dimers, $[(\text{TriEED})_2\text{X}_2(\mu\text{-CO}_3)\text{Cu}_2]$, are likely to be similar to previously described $[(\text{TEED})_2\text{Cl}_2(\mu\text{-CO}_3)\text{Cu}_2]$ [19], in which each copper(II) is coordinated by bidentate TEED and chloride. The coppers are bridged asymmetrically by a tridentate carbonate ligand, which leads to one copper being pentacoordinate and the other tetracoordinate [19].

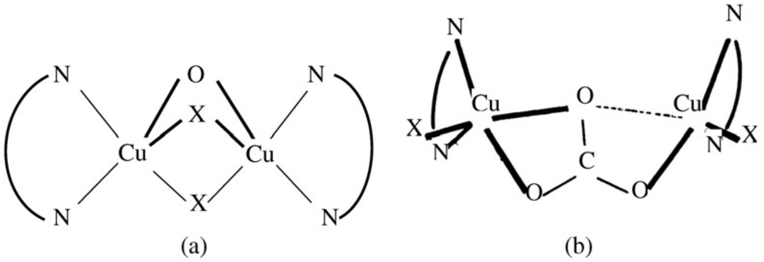
Analytical and cryoscopic data (table 1) for products of equations (4) and (5) establish the formation of discrete dimeric products.

3.2. *Infrared spectra*

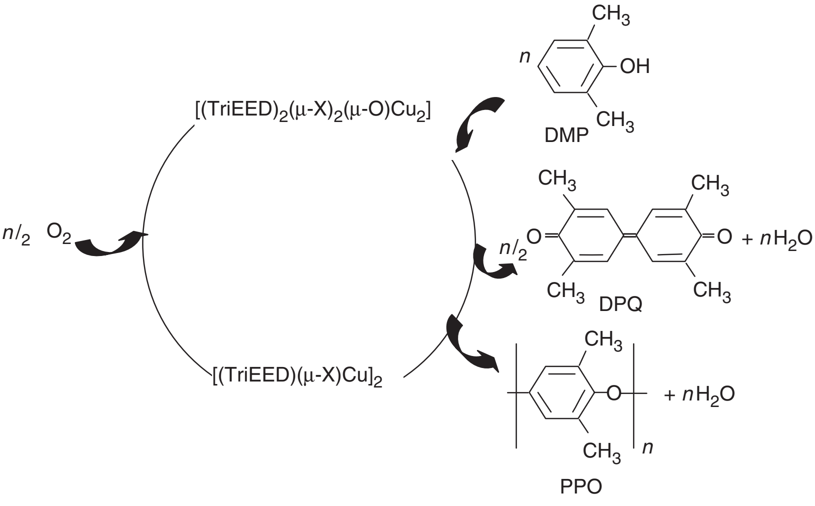
Major features of IR spectra of free TriEED, and $[(\text{TriEED})_2(\mu\text{-Cl})_2(\mu\text{-O})\text{Cu}_2]$ and $[(\text{TriEED})_2\text{Cl}_2(\mu\text{-CO}_3)\text{Cu}_2]$, show the following: (a) $\nu_{\text{N–H}}$ of free TriEED is two bands at 3375 and 3300 cm^{-1}; the one at lower wave number is more intense and shifted to (3437, 3173 cm^{-1}) and (3441, 3183 cm^{-1}) in $[(\text{TriEED})_2(\mu\text{-Cl})_2(\mu\text{-O})\text{Cu}_2]$ and $[(\text{TriEED})_2\text{Cl}_2(\mu\text{-CO}_3)\text{Cu}_2]$, respectively. (b) δ_{NH} of free TriEED shows a sharp, strong band at 1455 cm^{-1}. On complexation, it is split into two bands at 1465 and 1450 cm^{-1}. (c) For $[(\text{TriEED})_2\text{Cl}_2(\mu\text{-CO}_3)\text{Cu}_2]$, a new band at 1500 cm^{-1} and a more intense band at 740 cm^{-1} are attributed to bridging carbonato. (d) Both oxo and carbonato complexes show a new weak to medium intensity band at 490 cm^{-1} due to $\nu_{\text{Cu–O}}$ [19]. The above observations indicate that when bidentate TriEED is coordinated to the copper(II) center, the N–H vibrational modes are sensitive to coordination and the hydrogen atom of the secondary amine could undergo hydrogen bonding with any basic centers in $[(\text{TriEED})_2(\mu\text{-Cl})_2(\mu\text{-O})\text{Cu}_2]$ or $[(\text{TriEED})_2\text{Cl}_2(\mu\text{-CO}_3)\text{Cu}_2]$.

3.3. *Electronic spectra*

The room temperature electronic spectra of $[(\text{TriEED})_2(\mu\text{-X})_2(\mu\text{-O})\text{Cu}_2]$ and $[(\text{TriEED})_2\text{X}_2(\mu\text{-CO}_3)\text{Cu}_2]$ (X = Cl, Br or I) in methylene chloride exhibit broad bands with a long tail and maxima between 700 and 720 nm. Representative data are shown in table 2. The spectral ranges of these ligand field bands are characteristic of dimeric distorted five-coordinate copper(II) complexes [9, 19–21]. Due to the close



Scheme 2. Coordination of (a) μ-oxo [9] and (b) asymmetric μ-carbonato [19].



Scheme 3. Catalytic cycle for homogeneous oxidative coupling of phenols.

similarity of the spectra of the above complexes with [(TEED)$_2$(μ-X)$_2$(μ-O)Cu$_2$] and [(TEED)$_2$X$_2$(μ-CO$_3$)Cu$_2$] (X = Cl, Br or I) [9, 19, 20], in addition to the EPR activity (paramagnetism, see next), one can conclude a structural similarity between L = TriEED and TEED [18, 19] in both oxo and carbonato complexes (scheme 2).

3.4. *EPR spectra*

Room temperature solid state EPR spectra for [(TriEED)$_2$(μ-X)$_2$(μ-O)Cu$_2$] and [(TriEED)$_2$X$_2$(μ-CO$_3$)Cu$_2$] (X = Cl or Br), table 2, are axial with $g_{\parallel} > g_{\perp}$ in agreement with a $d_{x^2-y^2}$ ground state of a distorted square pyramid [22]. For both oxo and carbonato complexes when X = I, the spectra are isotropic with $g_i = 2.04$ and 2.07, respectively (table 2). Copper dimers normally exhibit a singlet-triplet ($\Delta M_s = \pm 2$) transition due to interaction between the two copper centers in dimeric complexes [19].

3.5. *Test of catalytic activity*

Solutions of [(TriEED)$_2$(μ-X)$_2$(μ-O)Cu$_2$] and [(TriEED)$_2$X$_2$(μ-CO$_3$)Cu$_2$], X = Cl, Br or I, in methylene chloride were added to separate samples of 100-fold excess of

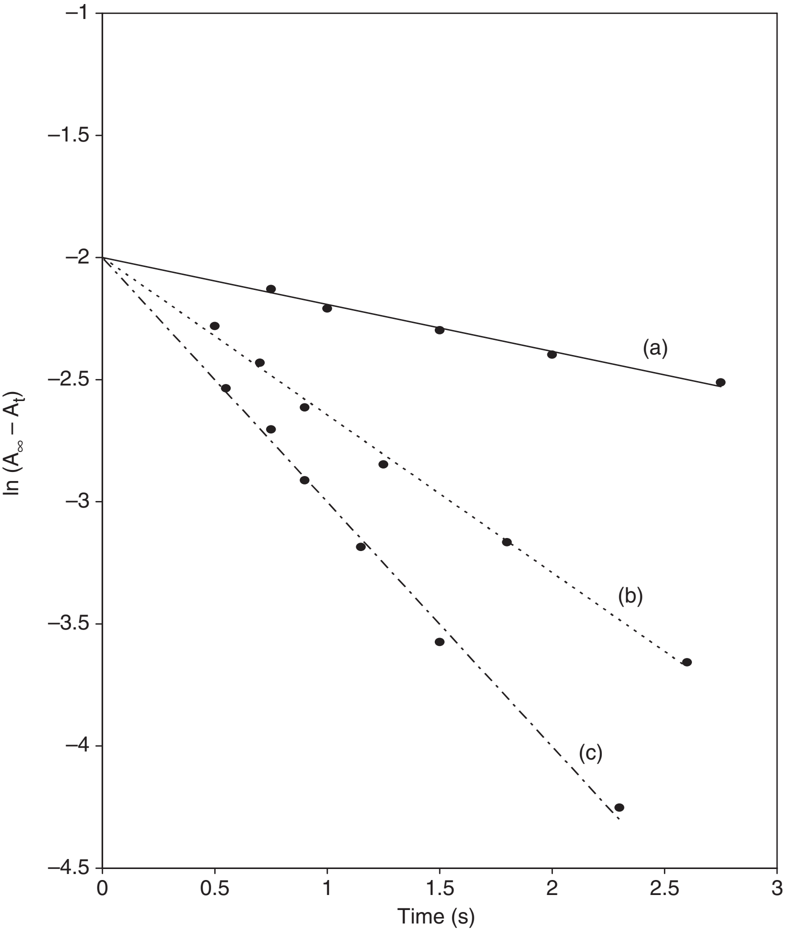


Figure 2. First-order plots for reaction of (a) 4.9×10^{-3} M, (b) 14.6×10^{-3} M and (c) 17.9×10^{-3} M $[(\text{TriEED})(\mu\text{-I})\text{Cu}]_2$ with dioxygen (4.4×10^{-3} M) in nitrobenzene at 27°C. Monitoring wavelength is 720 nm.

2,6-dimethylphenol in methylene chloride. Both oxo and carbonato complexes are reduced to the corresponding copper(I) complexes $[(\text{TriEED})(\mu\text{-X})\text{Cu}]_2$; then oxygen was bubbled through each solution for 20 min.

Two products are obtained, 3,3′,5,5′-tetramethyl-4,4′-diphenoquinone, DPQ (from C–C coupling), and poly-2,6-phenyleneoxide, PPO, (from C–O coupling), scheme 3.

When the substrate is only in 10-fold excess, the amount of PPO increases. When X = Cl, the amount of PPO increased relative to X = Br; for X = I, DPQ was the only product.

3.6. *Kinetics of oxidation of dimeric copper(I) complexes [(TriEED)(μ-X)Cu]₂, X = Br or I, by dioxygen in nitrobenzene*

Kinetic data for reactions of dioxygen with excess $[(\text{TriEED})(\mu\text{-X})\text{Cu}]_2$, X = Br or I, in nitrobenzene are easily monitored spectrophotometrically in the visible region, and the

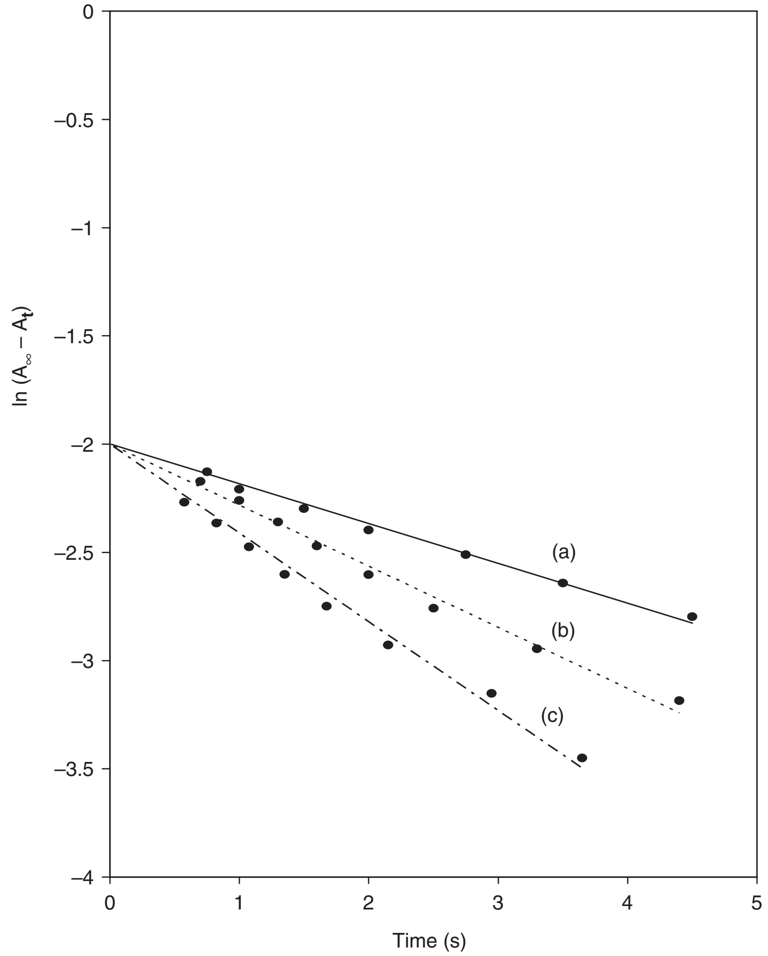


Figure 3. First-order plots for reaction of [(TriEED)(μ-I)Cu]$_2$ (4.9×10^{-3} M) with dioxygen (4.4×10^{-4} M) in nitrobenzene at (a) 27°C, (b) 36°C and (c) 58°C. Monitoring wavelength is 720 nm.

rates fall in conventional time domains. Where possible, a wide temperature range has been employed to allow estimation of activation parameters.

For excess [(TriEED)(μ-X)Cu]$_2$, X = Br or I, first-order plots of $\ln(A_\infty - A_t)$ *versus* time, where A_t is the absorbance of [(TriEED)$_2$(μ-X)$_2$(μ-O)Cu]$_2$ at time t, were linear for at least four half-lives (figures 1–3), indicating that the reaction is first order in [O$_2$].

Absorbances extrapolated to $t = 0$ correspond to those expected for copper(I) reactant at 700 and 720 nm for Br and I, respectively, thus providing no evidence for reactant pre-equilibria. The simple, first-order rate dependence indicates either that significant concentrations of intermediates are not formed, or that they do not absorb appreciably at the monitoring wavelengths.

The derived pseudo-first-order rate constants, k_{obsd}, were proportional to [[(TriEED)(μ-X)Cu]$_2$]^2, giving straight lines passing through the origin (figure 4). Reaction 5 is thus a third-order process, equation (6), when [(TriEED)(μ-X)Cu]$_2$ is in excess.

$$\mathrm{d}[[(\mathrm{TriEED})_2(\mu\text{-X})_2(\mu\text{-O})\mathrm{Cu}_2]]/\mathrm{d}t = k_{\mathrm{D}}[[(\mathrm{TriEED})(\mu\text{-X})\mathrm{Cu}]_2]^2[\mathrm{O}_2] \qquad (6)$$

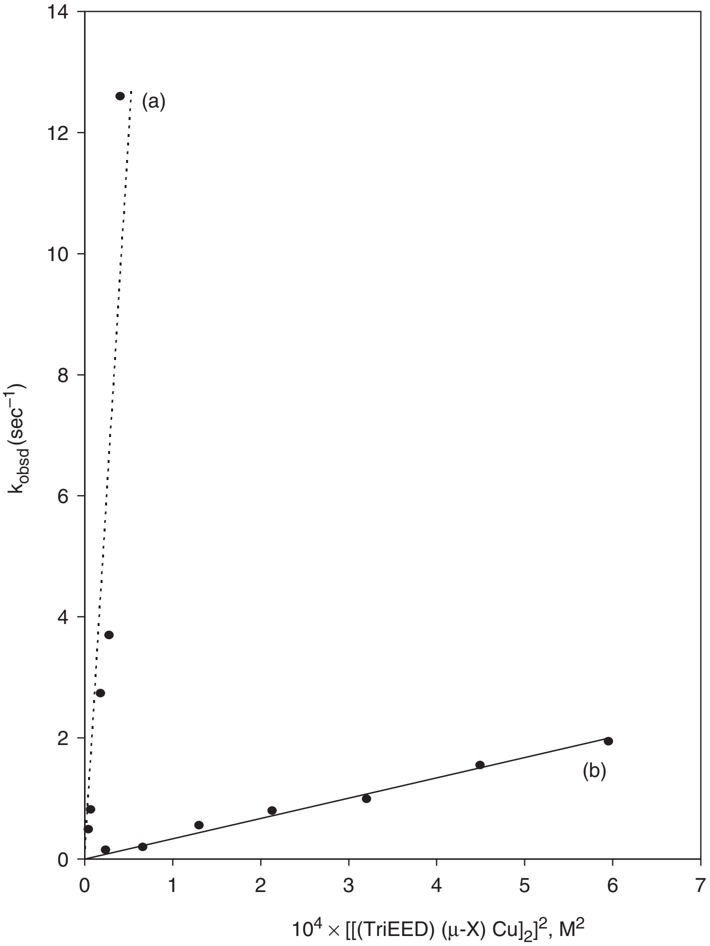


Figure 4. Dependence of the observed pseudo-first-order rate constant k_{obsd} on $[[(TriEED)(\mu\text{-}X)Cu]_2]^2$, where X = Br (a) and I (b) in nitrobenzene at 8°C for Br and 27°C for I. Monitoring wavelength is 700 nm for X = Br and 720 nm for X = I.

Third-order rate constant for dimeric copper(I) oxidation, k_D, and their activation parameters (determined from Eyring plots of $\ln(k_D/T)$ *versus* $1/T$) are listed in table 3.

3.7. *Features of the kinetic data*

The major features of the kinetic data for $[(TriEED)(\mu\text{-}X)Cu]_2$ oxidation by dioxygen in nitrobenzene are as follows:

(i) Small activation enthalpies are found for oxidation of $[(TriEED)(\mu\text{-}X)Cu]_2$, X = Br or I, indicating little structural rearrangement on activation of reactants. Negative activation entropies indicate substantial associative character in the activation process.

(ii) When X = Cl, the oxidation is too fast to be detected by conventional spectrophotometers.

Table 3. Kinetic parameters for $[(\mathrm{TriEED})(\mu\text{-X})\mathrm{Cu}]_2$, X = Br or I, oxidation by dioxygen in nitrobenzene, monitoring wavelength is 700 nm for X = Br and 720 nm for X = I.

Complex	Temp. (°C)	$10^{-5}\,k_D{}^a$	$\Delta H_D{}^{\neq b}$	$\Delta S_D{}^{\neq c}$
$[(\mathrm{TriEED})(\mu\text{-Br})\mathrm{Cu}]_2$	8	1.10		
	16	1.23		
	25	1.36		
	38	1.52		
	46	2.03		
	54	2.10	2.1	−28
$[(\mathrm{TriEED})(\mu\text{-I})\mathrm{Cu}]_2$	27	0.06		
	36	0.12		
	42	0.15		
	49	0.17		
	58	0.17	5.8	−22

[a] Units are $M^{-2}s^{-1}$, typical error is ±3%.
[b] Units are $\mathrm{kcal\,mol^{-1}}$, typical error is $\pm 0.2\,\mathrm{kcal\,mol^{-1}}$.
[c] Units are $\mathrm{cal\,deg^{-1}\,mol^{-1}}$, typical error is $\pm 3\,\mathrm{cal\,deg^{-1}\,mol^{-1}}$.

(iii) Changing X from Br to I decreases k_D by a factor of 20, while $\Delta H_D{}^{\neq}$ increases by a factor of 2.7 and $\Delta S_D{}^{\neq}$ increases by 20%. This difference is attributed to the higher stability of the copper(I) dimer when X = I and to a larger steric barrier of the iodo bridging over bromo, requiring more enthalpy to assemble the activated complex.

When one of the ethyl groups in TEED is replaced by H (TriEED), k_D increases by a factor of 220, $\Delta H_D{}^{\neq}$ decreases by a factor of 6 and $\Delta S_D{}^{\neq}$ increases by a factor of 9. Such large effects could only be due to lower steric effect for TriEED relative to TEED and to the presence of free N–H in TriEED, helping to assemble two dimers with dioxygen in the rate determining step through an intermolecular attractive force.

A linear plot of $\Delta H_D{}^{\neq}$ *versus* $\Delta S_D{}^{\neq}$ for all diamine ligands [8, 18], figure 5, can be constructed. The mechanism of oxidation of $[(\mathrm{TriEED})(\mu\text{-X})\mathrm{Cu}]_2$ with dioxygen is shown in equations (7)–(9).

$$[(\mathrm{TriEED})(\mu\text{-X})\mathrm{Cu}]_2 + \mathrm{O}_2 \xrightleftharpoons{K} [(\mathrm{TriEED})(\mu\text{-X})\mathrm{Cu}]_2 : \mathrm{O}_2 \tag{7}$$

$$\begin{aligned}&[(\mathrm{TriEED})(\mu\text{-X})\mathrm{Cu}]_2 : \mathrm{O}_2 + [(\mathrm{TriEED})(\mu\text{-X})\mathrm{Cu}]_2\\ &\xrightarrow[\text{R.D.S.}]{k_2} [(\mu\text{-O}_2)[(\mathrm{TriEED})_2)(\mu\text{-X})_2\mathrm{Cu(I)Cu(II)}]_2]\end{aligned} \tag{8}$$

$$\begin{aligned}&[(\mu\text{-O}_2)[(\mathrm{TriEED})_2)(\mu\text{-X})_2\mathrm{Cu(I)Cu(II)}]_2]\\ &\xrightarrow[\text{fast}]{} 2[(\mathrm{TriEED})_2(\mu\text{-X})_2(\mu\text{-O})\mathrm{Cu}_2]\end{aligned} \tag{9}$$

4. Conclusion

Copper(I) dimeric complexes with *N*,*N*,*N′*-triethylethylenediamine, TirEED, which has one N–H, reduce O_2 to the corresponding oxo complexes $[(\mathrm{TriEED})_2(\mu\text{-X})_2(\mu\text{-O})\mathrm{Cu}_2]$.

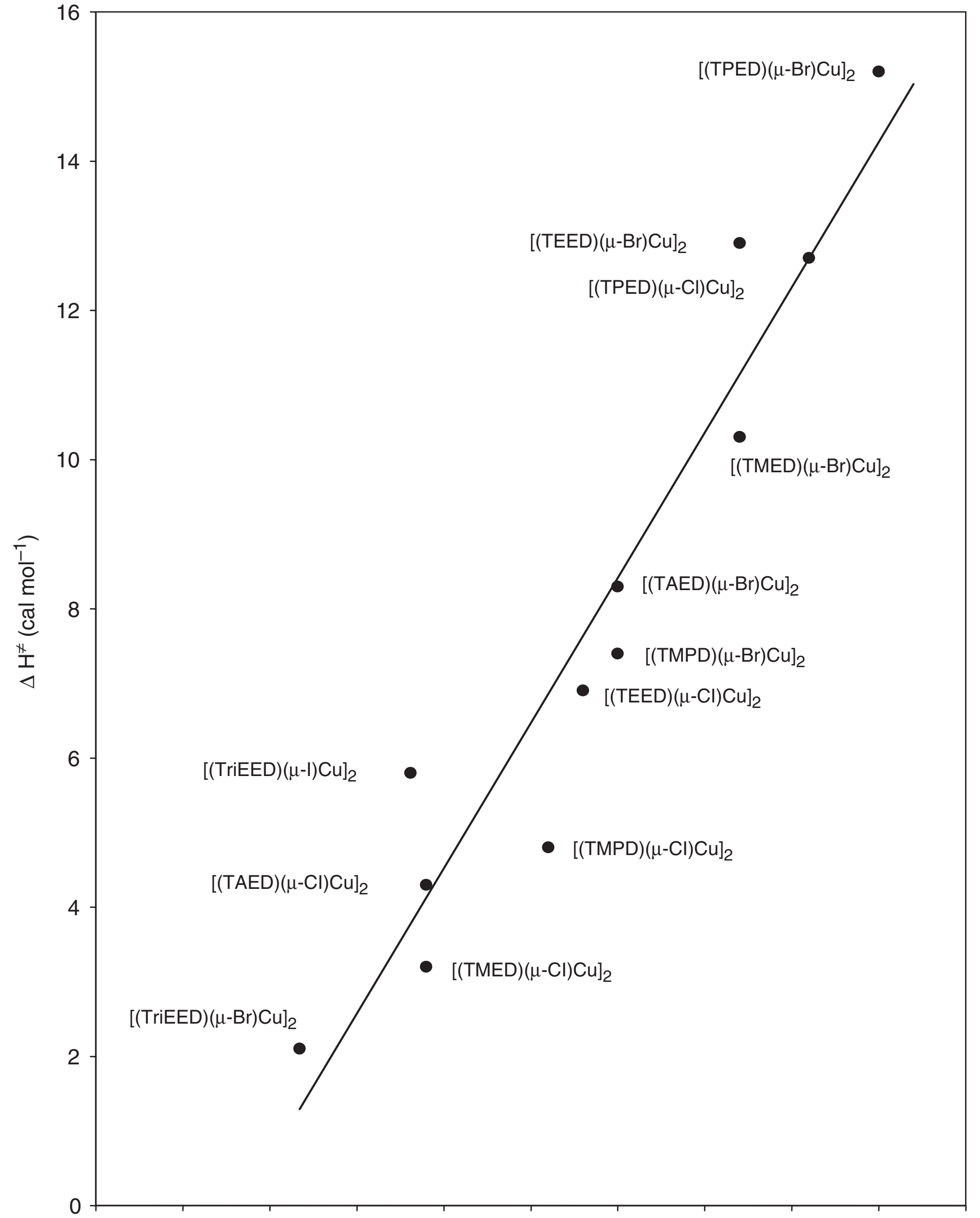


Figure 5. Plot of $\Delta H_D^{\neq}$ *vs.* $\Delta S_D^{\neq}$ for third-order oxidation of different diamine ligands on copper.

The N–H in TriEED helps assemble the two dimers of [(TriEED)(μ-X)Cu]$_2$ with dioxygen in the rate-determining step through an intermolecular attractive force.

Disproportionation and polymerization of [(TriEED)$_2$(μ-X)$_2$(μ-O)Cu$_2$] can be prevented by reaction with carbon dioxide to form the corresponding carbonato

$[(TriEED)_2X_2(\mu\text{-}CO_3)Cu_2]$ complexes. Both oxo and carbonato complexes are catalytically active for oxidation of 2,6-dimethylphenol.

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