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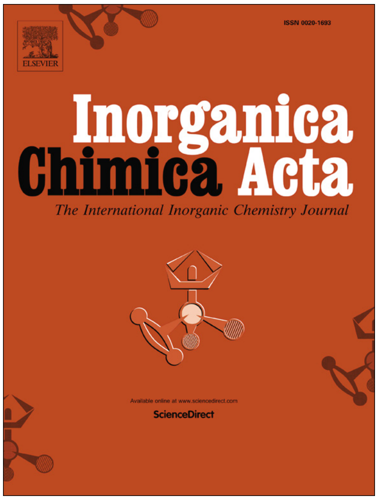

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Synthesis, Characterization, and Reactivity of Copper Complexes Supported by the TPMEN Ligand Framework

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KEYWORDS: Copper coordination chemistry, oxidation reactions, complex characterization, quinoline, pentadentate

ABSTRACT

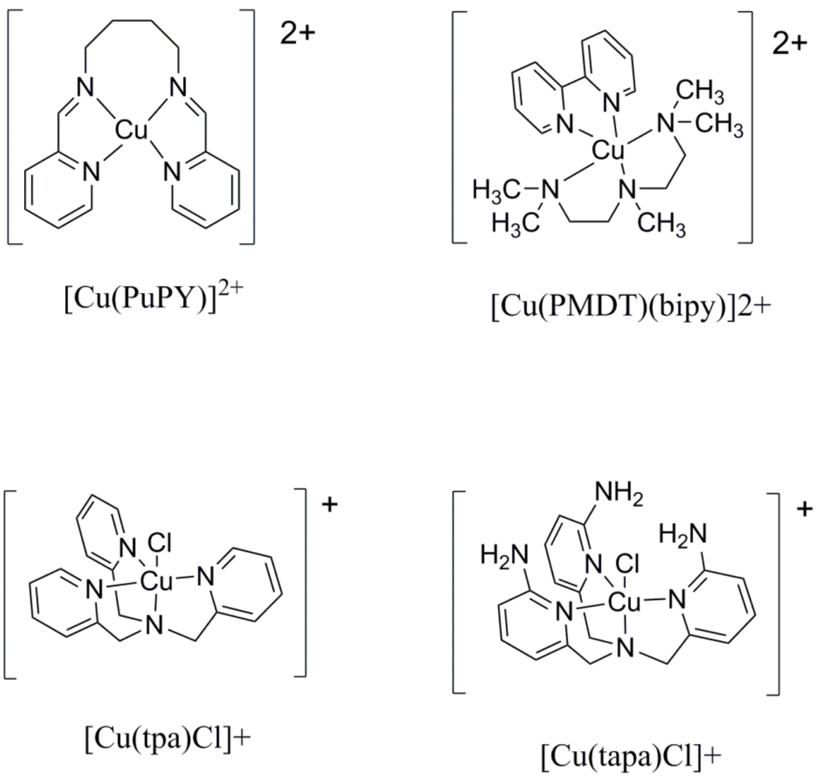
Two new Cu(II) complexes supported by nitrogen-rich ligands have been synthesized, and characterized by absorption spectroscopy, magnetic moment, and cyclic voltammetry. Complex **1** is supported by the ligand TPMEN (N,N,N'-tris(2-pyridylmethyl)-N'-methylethylenediamine) with two amine and three pyridyl nitrogen donors; while **2** is supported by the ligand TQMEN (N,N,N'-tris(2-quinolylmethyl)-N'-methylethylenediamine) where quinoline groups replace the pyridyl groups. Replacing the pyridyl moiety with quinoline has a marked effect on the Cu(II/I) reduction couple. The complexes are capable of reducing superoxide ($O_2^{\bullet-}$) to hydrogen peroxide (H_2O_2) in the presence of a proton donor. The reaction between potassium superoxide (KO_2) and the Cu-complexes was monitored via absorption spectroscopy, and further probed with electrospray ionization mass spectrometry (ESI-MS). Both **1** and **2** depicted evidence of ligand oxidation in mass-spectrometry.

INTRODUCTION

Transition metal complexes supported by pentadentate polypyridyl ligands have been widely studied in literature because of their diverse applications in synthetic and bioinorganic chemistry.[1-8] In particular, Cu-complexes supported by pentadentate N5 ligands have applications in substrate oxidation,[9] water oxidation catalysts,[2,10,11] modeling enzyme activity,[12] and cleavage of plasmid DNA.[13] Very recently, a Cu-complex supported by the pentadentate N5 bztpen (N-benzyl-N,N',N" –tris(pyridine-2ylmethyl)ethylenediamine) ligand was reported.[10] The ligand architecture played a crucial role in the complex reactivity as it was observed that modifying bztpen with more benzyl moieties increased its oxygen-evolving capabilities.[11] Another ligand of the N5 ligand family, the N4Py ligand (N,N-bis(2-pyridylmethyl)-N-bis(2-pyridyl)methylamine) and its bulkier analogue in which two pyridine rings of the ligand were replaced by quinoline groups (2PyN2Q) supported Cu-complexes showed a difference in substrate binding modes and changes in reduction potential.[14] Thus, it can be stated that ligand electronics and bulk of the ligand have a strong effect on the properties of the supported metal complex.[4,14,15]

Studying properties and reactivity of pentadentate mononuclear Cu(II)-complexes is biologically relevant as it mimics the oxidized state of the active site of CuZnSOD. The CuZn superoxide dismutase (CuZnSOD) enzyme is an excellent model system for Cu-O_2 chemistry as the enzyme controls the dismutation of superoxide ($O_2^{\bullet -}$) to hydrogen peroxide (H_2O_2) and molecular oxygen (O_2).[16] Human SOD1 is a homodimeric protein with each subunit holding one copper and one zinc binding site. In the reduced form, Cu(I) is ligated by His46, His48, and His120 in a nearly trigonal planar geometry while the zinc is coordinated nearby with His63, His71, His80, and Asp83. Upon oxidation to Cu(II), His63 bridges the Cu(II) ion to the zinc ion while a water molecule also binds to the copper resulting in a five-coordinate copper with distorted square pyramidal geometry.[16] Several model complexes have been synthesized to mimic the spectroscopic, structural, and catalytic properties of CuZnSOD. The dismutation activity of these model complexes were correlated to the flexibility of the geometric transformations at the copper center during the Cu(II)/Cu(I) redox process during catalysis.[17-20]

Structural models of the enzyme were synthesized with hetero and homo dinuclear imidazolate-bridging complexes and they exhibited excellent SOD activity.[20,21] In the enzyme, CuZnSOD, the metal center that participates in red-ox processes is the Cu-center. As a result, attempts were made to design functional mimics of the enzyme with mononuclear copper complexes.[17,22-25] However, in these functional mimics reactivity showed strong dependence on coordination geometry around the metal center. The tetradentate complex $[Cu(PuPy)](ClO_4)_2$ with square planar geometry showed moderate SOD activity[26], while the tetradentate complexes $[Cu(tpa)(H_2O)](ClO_4)_2$ and $[Cu(tapa)Cl]ClO_4$ with trigonal bipyramidal geometry exhibited relatively high SOD activity (Figure 1).[23] The pentadentate complex $[Cu(PMDT)(bipy)](ClO_4)_2$ with distorted square pyramidal geometry has shown moderate SOD activity (Figure 1).[25] While there is a large body of work devoted to CuZnSOD mimics,[17,22,23,27-31] the study of pentadentate nitrogen-rich ligands as support for CuZnSOD models has not been thoroughly explored.



$[Cu(PuPY)]^{2+}$

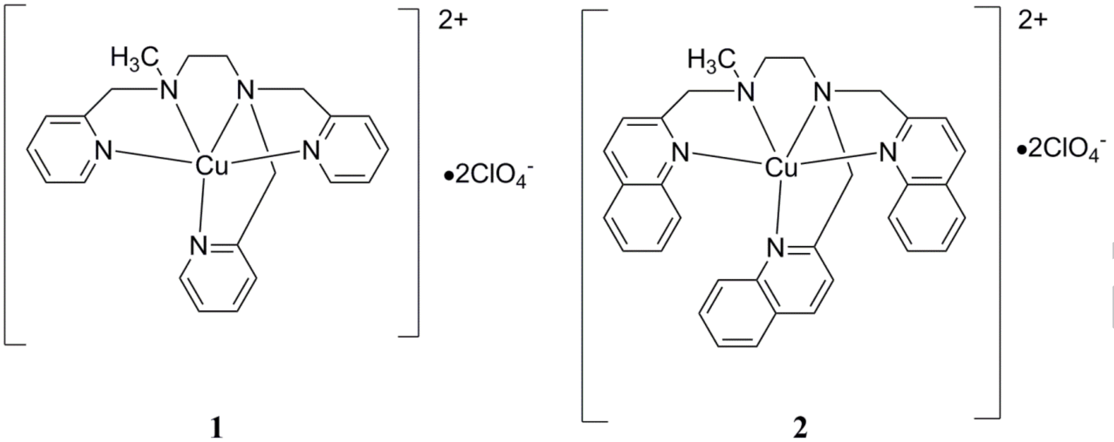
$[Cu(PMDT)(bipy)]2+$

$[Cu(tpa)Cl]+$

$[Cu(tapa)Cl]+$

Figure 1. Structures of N-polydentate Cu-complexes that have shown SOD activity: (top left) $[Cu(PuPY)]^{2+}$ (PuPY =1,8-Bis(2-pyridyl)-2,7-diazaoctadiene-1,7), (top right) $[Cu(PMDT)(bipy)]^{2+}$ (PMDT = N,N,N',N'',N''-pentamethyldiethylenetriamine, bipy = 2,2'-bipyridine), (bottom left) $[Cu(tpa)Cl]^{+}$ (tpa = tris(2-pyridylmethyl)amine), and (bottom left) $[Cu(tapa)Cl]^{+}$ (tapa = tris(6-amino-2-pyridylmethyl)amine).

This paper reports the synthesis and characterization of two novel Cu-complexes supported by neutral N5 ligands, $[Cu(TPMEN)(ClO_4)_2]$ and $[Cu(TQMEN)(ClO_4)_2]$ (Figure 2). It was noticed that substituting quinoline-N donors for pyridine-N donors affects the redox potential of the ligated metal as noted in the literature.[32] The reactivity of $[Cu(TPMEN)(ClO_4)_2]$ and $[Cu(TQMEN)(ClO_4)_2]$, hereafter referred to as **1** and **2** respectively, were investigated towards potassium superoxide at ambient temperatures.



1 **2**

Figure 2. Proposed structures of [Cu(TPMEN)(ClO$_4$)$_2$] (**1**) and [Cu(TQMEN)(ClO$_4$)$_2$] (**2**).

EXPERIMENTAL METHODS

Materials N,N,N'-tris(2-pyridylmethyl)-N'-methylethylenediamine (TPMEN) and N,N,N'-tris(2-quinolylmethyl)-N'-methylethylenediamine (TQMEN) were synthesized according to reported procedures.[33,34] **Caution!** Although no problems were encountered in the preparation of the perchlorate salts, care should be taken when handling such potentially hazardous compounds. The reagents and the solvents used in this study, except for the ligands and complexes, were commercially available and obtained in the highest available purity from Sigma-Aldrich and Fisher Scientific. ^{1}H NMR experiments were performed in deuterated solvents purchased from Cambridge Isotope Laboratory on a Varian Inova-500 MHz instrument at 25 °C. UV-visible experiments were performed on an Agilent Cary 8454 UV-visible spectrometer in a quartz cuvette with a 1 cm pathlength. Electrochemical measurements were carried out on a BASi-C3 Epsilon electrochemical instrument using a glassy carbon working electrode, a platinum wire auxiliary electrode, and Ag/AgCl reference electrode. All cyclic voltammetric experiments were performed under nitrogen atmosphere using tetrabutyammonium hexafluorophosphate (TBF-6, 0.1M) as the supporting electrolyte. Electrospray ionization mass spectrometry (ESI-MS) experiments were performed on a Thermo Scientific LTQ Orbitrap XL Hybrid FT Mass Spectrometer in positive ionization mode. ESI-MS measured with an ion transfer tube temperature of 240 °C and a flow rate of 5 μL. Solid state magnetic susceptibility measurements were performed at room temperature using a MSB Evan's balance (model number MK I #7967; Johnson Matthey; Wayne, PA). The appropriate diamagnetic corrections were applied using Pascal's constants.[35] Elemental analyses were performed by Atlantic Microlab, Inc (Norcross, GA).

Synthesis of N,N,N'-tris(2-pyridylmethyl)-N'-methylethylenediamine (TPMEN)

2-Picolyl chloride hydrochloride (3.0 g, 18.3 mmol) was dissolved in 10 N NaOH (30 mL) aqueous solution. To this solution, N-methylethylenediamine (0.45 mL, 5.2 mmol) was added dropwise with stirring. After stirring for 3 days at room temperature, the upper oil layer was decanted and dissolved in dichloromethane (30 mL). The dichloromethane solution was washed with an excess of water (80 mL) and dried using anhydrous $MgSO_4$. After evaporation of dichloromethane, the crude sample was purified using a silica column ($CHCl_3$:CH_3OH 10:1 (v/v)). A light brown oil was obtained with a 50% yield (0.90 g, 2.6 mmol). NMR δ (500 MHz, $CDCl_3$) 8.51 (m, 3H, -Py), 7.62 (m, 3H, -Py), 7.52, 7.37 (m, 3H, -Py), 7.13 (m, 3H, -Py), 3.85 (s, 4H, $-N(-CH_2-Py)_2$), 3.48 (s, 2H, $-N-CH_2-Py$), 2.77 (d, 4H, $N-CH_2CH_2-N$), 2.20 (s, 3H, $-CH_3$).

Synthesis of N,N,N'-tris(2-quinolylmethyl)-N'-methylethylenediamine (TQMEN)

2-(chloromethyl) quinoline hydrochloride (3.0 g, 14.01 mmol) was dissolved in 10 N NaOH (30 mL) aqueous solution. To this solution, N-methylethylenediamine (0.347 mL, 3.98 mmol) was added dropwise with stirring. After 3 days at room temperature, the upper oil layer was decanted and dissolved in dichloromethane (30 mL). The dichloromethane solution was washed with an excess of water (80 mL) and dried using anhydrous $MgSO_4$. After evaporation of dichloromethane, the crude sample was purified using a silica column (CH_2Cl_2:CH_3OH 10:1 (v/v)). Light yellow oil of the ligand was obtained with 67% yield (1.3 g, 2.7 mmol). ^1H NMR δ (500 MHz, $CDCl_3$) 8.09 (m, 3H, -Qn), 8.01 (m, 3H, -Qn), 7.86 (m, 3H, -Qn), 7.80 (m, 3H, -Qn), 7.65 (m, 3H, - Qn), 7.55 (m, 3H, -Qn), 5.65-5.36 (d, 4H, N-CH_2CH_2-N), 4.28 (s, 3H, -CH_3), 3.48 (s, 4H, -N(-CH_2-Qn)$_2$), 3.40 (S, 2H, -N-CH_2-Qn). ^{13}C NMR (500 MHz. $CDCl_3$) 158.68, 150.41, 147.45, 137.57, 136.76, 130.15, 129.67, 129.20, 128.96, 127.83, 127.70, 127.62, 127.22, 126.44, 125.03, 121.23, 65.56, 61.28, 57.84, 48.93. ESI-MS *m/z* for $[TQMEN + H]^+$: 498.27 (calculated), 498.25 (experimental, $[L+H]^+$).

Complex Syntheses

Both **1** and **2** were prepared by reaction of $[Cu(ClO_4)_2]\bullet 6H_2O$ with TPMEN or TQMEN, respectively, in a 1:1 mole ratio in methanol. Solutions were stirred at room temperature for 30 min before the precipitate was filtered. The precipitates were washed with cold water (1 mL) and diethyl ether (1 mL) before being dried *in vacuo*.

$[Cu(TPMEN)(ClO_4)_2]$ (1) Mixing methanol solutions of TPMEN (0.256 g, 0.737 mmol) and $[Cu(ClO_4)_2]\bullet 6H_2O$ (0.274 g, 0.740 mmol) yielded a royal blue solid (0.274 g, 0.450 mmol, yield: 61%). ESI-MS *m/z* for $[Cu(TPMEN)(ClO_4)]^+$: 509.09 (calculated), 509.17 (experimental). Elemental analysis calculated for $[Cu(TPMEN)(ClO_4)_2]\bullet 2H_2O$: C, 38.57; H, 3.92; N, 10.70; Cl, 11.49%. Found: C, 39.05; H, 4.35; N, 10.84; Cl, 10.98%. UV-vis (λ (nm) [ε ($M^{-1}cm^{-1}$)] in MeCN at 25 °C: 682 (279), 907 (130).

[Cu(TQMEN)(ClO_4)$_2$] (2) Mixing methanol solutions of TQMEN (0.225 g, 0.452 mmol) and [Cu(ClO_4)$_2$]•6H_2O (0.107 g, 0.451 mmol) yielded a mint green solid (0.239 g, 0.316 mmol, yield: 70%). ESI-MS *m/z* for $[Cu(TQMEN)]^{2+}$: 280.25 (calculated), 279.67 (experimental). Elemental analysis calculated for [Cu(TQMEN)(ClO_4)$_2$]•2H_2O•HCl: C, 47.68; H, 4.05; N, 7.72; Cl, 12.27%. Found: C, 47.61; H, 4.36; N, 8.41; Cl, 12.77%. UV-vis (λ (nm) [ε ($M^{-1}cm^{-1}$)] in MeCN at 25 °C: 745 (206).

Potassium superoxide reactivity

A solution of **1** (2 mM) in a dry solution of acetone/DMF (4:1 v/v) was allowed to react with one equivalent KO_2. The stock solution of KO_2 (50 mM) was prepared in the same solvent system using equimolar amounts of 18-crown-6 to solubilize KO_2. The reaction mixture was stirred at 25 °C for 3.5 hours. The procedure was the same for **2**, except the reaction was allowed to stir for 6 hours.

Demetallation of reaction products

Demetallation studies were carried out as previously reported.[36] The reaction mixture was treated with NH_4OH (5 ml) and passed through an alumina column. The alumina column was washed with methanol (50 ml) followed by dichloromethane (80 ml). The combined filtrate was washed with water (3 x 20 ml). The organic phase was dried over Na_2SO_4 and concentrated *in vacuo*.

Quantification of liberated hydrogen peroxide (H_2O_2)

Amount of hydrogen peroxide was determined by iodometry as follows. To a solution of **1** (2 mM) in a dry solution of acetone/DMF (4:1 v/v) two equivalents of $HClO_4$ were added followed by the addition of one equivalent KO_2 at room temperature (18-crown-6 was used to solubilize KO_2). After completion of the reaction, another two equivalents of $HClO_4$ was added to stabilize the liberated hydrogen peroxide. Then 1 mL of this final reaction mixture was diluted to 10 mL and was treated with excess NaI. The amount of I_3^- liberated was quantified using UV-visible spectroscopy (λ_{max}= 361 nm, $\varepsilon = 2.5 \times 10^4$ M^{-1} cm^{-1}). The procedure is the same for **2**.

RESULTS AND DISCUSSION

Synthesis and Characterization

The synthesis of the N5 ligands was accomplished following the published procedure known for respective ligands.[33,34] The Cu-complexes, $[Cu(TPMEN)(ClO_4)_2]$ (**1**) and $[Cu(TQMEN)(ClO_4)_2]$ (**2**), were synthesized by adding one equivalent $Cu(ClO_4)_2 \bullet 6H_2O$ to the respective ligands in methanol. This is the first report of these complexes in literature. The complexes were characterized by various analytical and spectroscopic techniques. Both **1** and **2** were soluble in polar solvents such as acetonitrile and acetone, but sparingly soluble in nonpolar solvents. The optical spectra for the Cu-complexes in acetonitrile and methanol are shown in Figure 3, while the optical parameters along with molar absorptivity in methanol, acetone, and acetonitrile are summarized in Table 1. Both complexes exhibited a low intensity band between 600-800 nm. Complex **1** exhibited a broad peak at 682 nm in acetonitrile along with a shoulder in the 908 nm region. The peak of **1** appeared in a similar position in methanol and acetone (Table 1). Complex **2** had a peak at 745 nm in acetonitrile, which was shifted to a higher wavelength in methanol and acetone. The red shift in the peak position of **2** compared to **1** is similar to other known Cu-complexes where pyridyl groups in the ligand were replaced by quinoline groups.[14,37] The optical spectral data of complex **1** and **2** matched well with other reported Cu-complexes supported by N5 ligands with distorted trigonal bipyramidal geometry.[14,38]

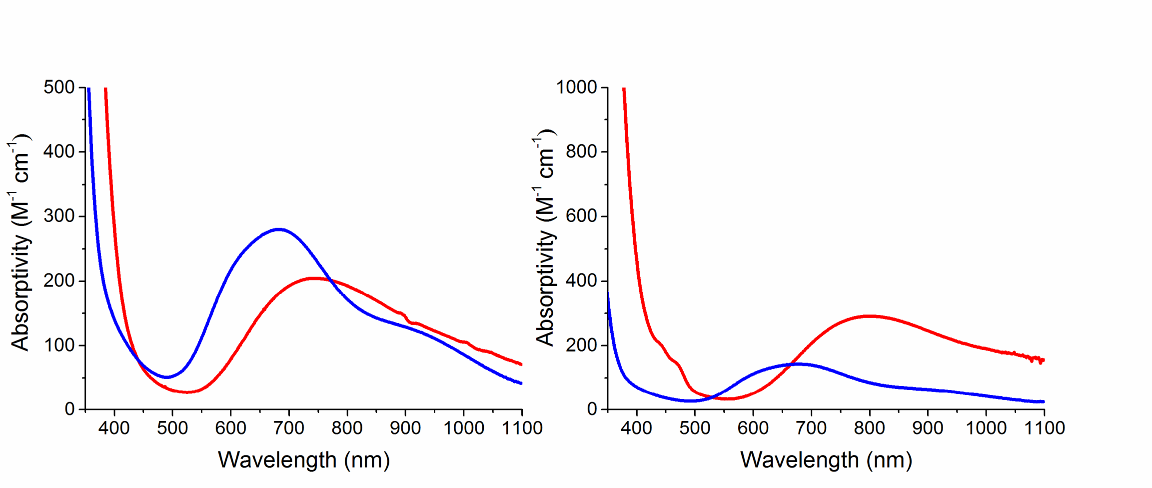


Figure 3. Optical data of **1** (Blue solid line) and **2** (Red solid line) in acetonitrile (left) and methanol (right). Data were collected at room temperature using a cuvette with 1 cm pathlength.

Table 1: Optical and magnetic parameters of the Cu(II) complexes.

Compound	**Optical Parameters** λ (nm), [ε ($M^{-1}cm^{-1}$)]			**Magnetic Parameters**	
	Methanol	**Acetonitrile**	**Acetone**	μ_{eff} (B.M.)	χ_A (emu mol^{-1})
1	668 (144), 910 sh	682 (278), 907 sh	676 (384), 900 sh	1.84	1.11 x 10^{-3}
2	800 (292), 440 sh, 472 sh	745 (206)	772 (189), 441 sh, 471 sh	1.82	9.97 x 10^{-4}

The magnetic susceptibility of both complexes was measured in an Evans Balance at room temperature. Complex **1** has a magnetic moment of 1.84 B.M, and **2** has a magnetic moment of 1.82 B.M. These values lie within the expected range for a Cu(II) complex,[39] as well as being similar in value to other pentadentate mononuclear Cu(II) complexes.[40] Based on the electronic spectra of related complexes and magnetic susceptibility measurements, it can be concluded that **1** and **2** exist as mono-nuclear complexes with distorted trigonal bipyramidal geometry.[10,38]

The cyclic voltammogram (CV) of **1** exhibited a quasi-reversible redox peak corresponding to the Cu(II)/Cu(I) couple at $E_{1/2}$ = – 0.13 V (versus Ag/AgCl, ΔE = 90mV, Figure 4), near that of similar Cu(II) complexes supported by pyridine N-donor ligands.[10,11] The peak current increased proportionally to the square root of the scan rate, as it was varied from 100 mV/s to 500 mV/s suggesting a diffusion-limited single electron transfer reaction. The CV of **2** had a more positive reduction potential than **1** with a cathodic peak at + 0.55 V and an anodic peak at – 0.15 V (versus Ag/AgCl, Figure S1). This trend of a more positive reduction of Cu(II) supported by quinoline ligands compared to pyridine ligands had been noted in literature.[14,32,38] This electrochemical trend is likely due to the relative base strength of the quinoline N donors versus pyridine N donors.[32,41]

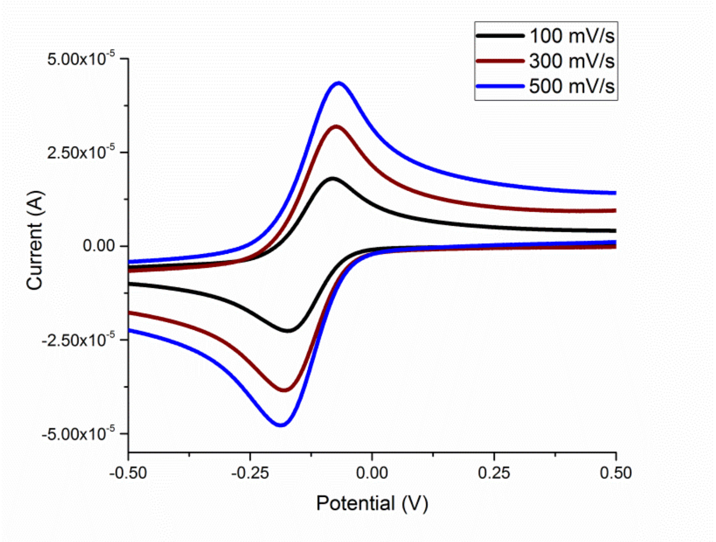


Figure 4. Cyclic voltammogram of **1** in DMF under N_2 with 0.1 M TBF-6 as the supporting electrolyte.

Analysis of Superoxide Reduction

The reduction potential of **1** and **2** lie within the window for superoxide disproportionation (-0.18 V and +0.91 V).[42] Both complexes were investigated for superoxide reduction capabilities. When **1** and **2** were subjected to react with superoxide in the presence of a proton source, production of hydrogen peroxide was quantified via sodium iodide (NaI) assays. The reaction of NaI with hydrogen peroxide produces I_3^-, which has a λ_{max} of 361 nm, and can be monitored with UV-visible spectroscopy (see Figures S2 and S3). Perchloric acid acts to stabilize the hydrogen peroxide, thus to insure a more accurate assay. Both **1** and **2** produce hydrogen peroxide with moderate yield (40% and 41 %, respectively). In the absence of Cu, the percent yield of hydrogen is negligible (0.03 %). Thus, the Cu-complexes are key facilitators in the reduction of superoxide to hydrogen peroxide, which is not surprising as it is known that Cu(II)-superoxide model complexes are nucleophilic in nature and tend to form more stable cupric-hydroperoxo intermediate if proton source is available. Furthermore, this hydroperoxo intermediate can undergo various decay pathways, but in the presence of a proton source like perchloric acid it can be further protonated to produce hydrogen peroxide. The moderate yield of hydrogen peroxide production, however, suggests possible side reactions are also occurring. In order to understand what other possible decay pathway may impede the hydrogen peroxide yield, UV-visible spectroscopy was used to monitor the reaction between the Cu-complexes and KO_2 in absence of a proton source.

Monitoring reactivity with potassium superoxide using optical spectroscopy

The reaction between both **1** and $KO_2/HClO_4$ produced no color change (Figure S4), **2** behaved similarly. However, in the absence of perchloric acid, the reaction with one equivalent KO_2 in dry acetone/DMF produced a color change for both **1** and **2**. Both complexes reacted rapidly with KO_2 as evidenced by a swift color change from royal blue to emerald green for **1** and green to yellow for **2** (Figure 5). Optical spectra of **1** in dry acetone/DMF (4:1 v/v) showed two characteristic features, a broad band in 600-700 nm and an intense peak at 330 nm. Upon the addition of one equivalent KO_2 to **1**, the peak at 330 nm exhibited an immediate increase in intensity along with slight shift to 340 nm. The band in the 600-700 nm decayed simultaneously. The peak at 340 nm lost its intensity over time (3.5 hours). Similarly, **2** showed a peak at 340 nm in the acetone/DMF solvent mixture along with a broad band in 800 nm. Upon addition of KO_2 the band at 800 nm decreased its intensity but the peak at 340 nm slightly increased in intensity (Figure 5, right panel). Over time, the peak at 340 nm decayed to generate an optical spectrum with a shoulder at 420 nm. The final solution of each reaction was analyzed with electrospray ionization mass spectrometry (ESI-MS). Evidence for ligand oxidation was observed in the ESI-MS spectrum for **1**, a peak emerged at 424 *m/z* (Figures S5-S6). Simulation of the peak *at m/z* 424 indicated oxidation of the ligand in one of the benzylic position (Figure S6). Removing the Cu from the product solution afforded brown oil. Analysis of this brown oil with ESI-MS showed two peaks at *m/z* 348 and 362 corresponding to TPMEN and oxidized TPMEN, respectively (Figures S7-S8). When the final solution of **2** and KO_2 was analyzed, a new peak at *m/z* 574 was detected. The isotope pattern of this peak also closely matched with the simulated data (Figures S9-S10). ESI-MS analysis of the product solution after removing Cu revealed a peak at *m/z* 512 attributed to oxidized TQMEN (Figures S11-S12).

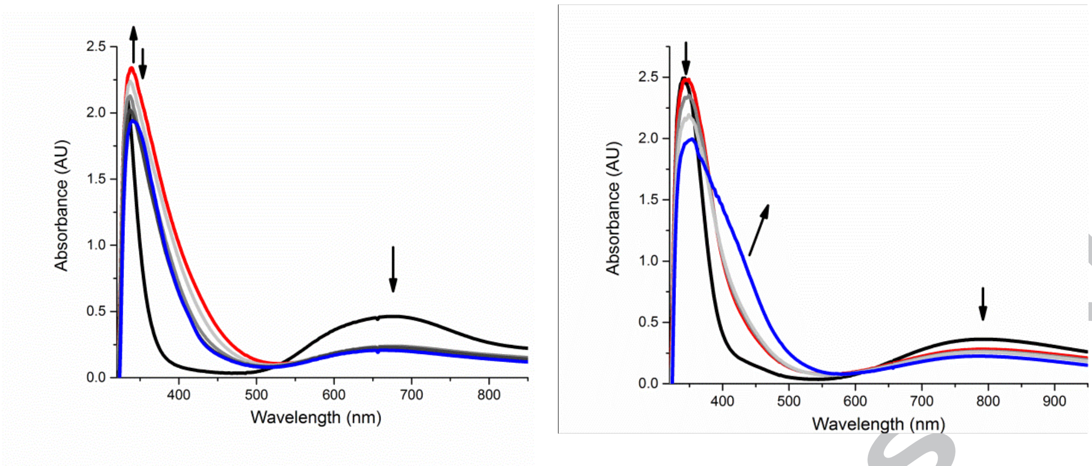
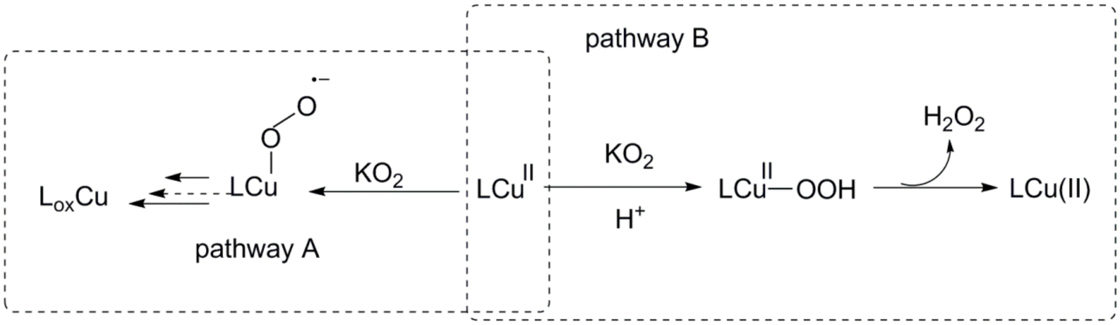


Figure 5. Optical changes of **1** and **2** with 1 equiv. KO_2 in acetone/DMF (4:1) at RT using 1 cm pathlength. Left panel showed the reaction of **1** and right panel showed reaction of **2**. In both cases: black is the starting material, red trace is generated upon immediate addition of KO_2, and blue line reflect the final spectrum.

Scheme 1. Possible pathways for superoxide reaction with Cu-complexes



CONCLUSION

This is the first report of the synthesis and reactivity of mononuclear Cu(II) complexes [Cu(TPMEN)(ClO_4)$_2$] and [Cu(TQMEN)(ClO_4)$_2$]. The complexes were characterized using spectroscopic and analytical techniques. The electrochemistry of the Cu-complexes was in accord with previously reported complexes. Both **1** and **2** demonstrated the ability to reduce superoxide to hydrogen peroxide as confirmed by sodium iodide assays. The reduction yields were moderate for both Cu-complexes. This led to the investigation of possible side reactions between the Cu-complexes and KO_2 via UV-visible spectroscopy and ESI-MS. The evidence of ligand oxidation by mass-spectrometry suggested that the reaction of **1** and **2** with superoxide have multiple pathways to progress. In the presence of a proton source, superoxide can bind to the Cu-center and get further reduced to cupric hydroperoxo intermediate. The protic medium facilitates production of hydrogen peroxide from this intermediate (Scheme 1, pathway B). However, in the absence of proton the Cu(II)-superoxide intermediate might abstract a proton from the ligand and generate reactive intermediates species that further oxidize the ligand (Scheme 1, pathway A). Reactivity of Cu-superoxide species is very different, in some examples Cu-superoxide showed abstraction of H-atom from ligand,[43] but in other case cupric-hydroperoxo (Cu-hydroperoxo) seems to be the stronger oxidant.[44] In literature, the absorption region of 325-465 nm was associated before with Cu-hydroperoxo complexes supported by polypyridyl ligands.[45-47] Thus, the peak seen in the spectrum of **1** and **2** upon addition of KO_2 at ~340 nm could be indicative of a Cu-hydroperoxo intermediate that oxidizes the ligand.[45,46] At this stage, the mechanism for both pathways remain unclear. Pathway B could happen via Fenton chemistry involving a hydroxyl radical, or some other metal-based oxidant. Clearly, further work is warranted to determine the intermediate and establish mechanism of the reaction between these Cu-complexes and KO_2. Current research in the group focuses in that direction.

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Notes

The authors declare no competing financial interest

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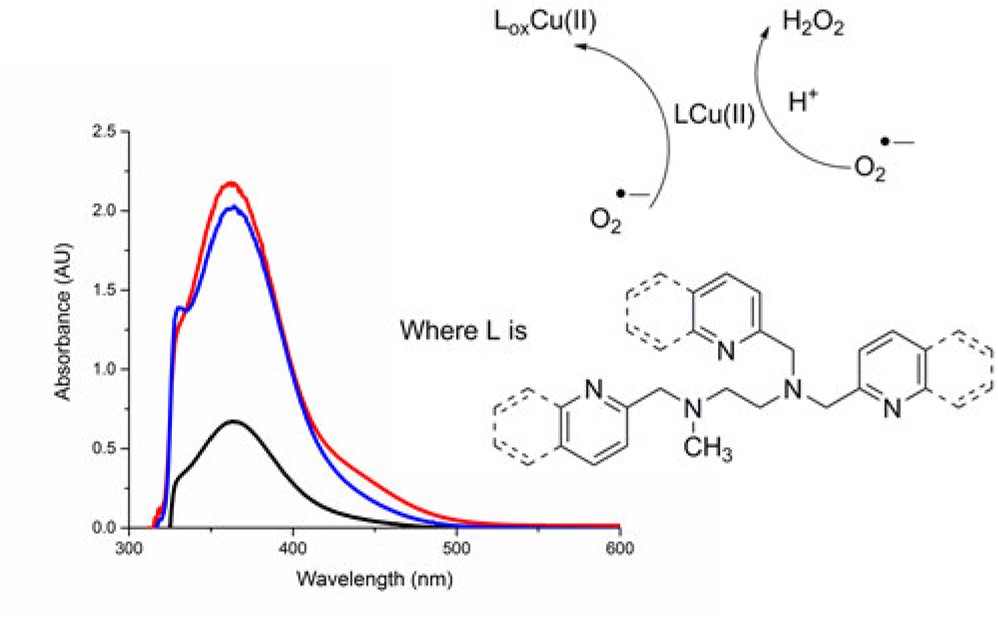
Highlight:

- Nitrogen-rich, pentadentate Cu(II) complexes were synthesized and characterized by absorption spectroscopy, cyclic voltammetry, and magnetic moment.
- Reactivity with potassium superoxide (KO_2) was monitored with UV-Visible spectroscopy.
- The Cu complexes were capable of reducing superoxide to hydrogen peroxide in the presence of a proton donor.


$L_{ox}Cu(II)$
H_2O_2
LCu(II)
H^+
$O_2^{\bullet -}$
$O_2^{\bullet -}$
Where L is
N
N
N
N
N
CH_3
2.5
2.0
1.5
1.0
0.5
0.0
Absorbance (AU)
300
400
500
600
Wavelength (nm)