sections. (These contain all independent atoms in structures composed of close-packed planes perpendicular to the *c* axis.) Figure 1a shows that Li$_{0.09}$YCl is derived directly from YCl (also $R\bar{3}m$) by random substitution of lithium in about 20% of the TAP interstices between double-chlorine layers. A clear decrease of 0.023 (3) Å in the interlayer Y–Y distance accompanies reduction of the slabs, though increasing Y–Cl and Cl–Cl separations caused an overall increase in *c*. Isostructural Li$_x$GdCl has also been found recently.[11]

A carbide M′ClC$_{0.5}$, M′ = Sc, Y, analogous to ZrClO$_{0.4}$ is also stable, but in this case, the phase appears stoichiometric and the size of the non-metal requires substitution in TAP, not tetrahedral positions between the double-metal layers. Second-nearest-neighbor interactions appear responsible for the reordering of the layers into a one-slab repeat structure, Figure 1e. The isostructural compound ZrXC$_{0.5}$ also forms with ZrCl and ZrBr.[12]

Alkali-metal intercalates are also formed with interstitial (tetrahedral) oxygen in both 3R- and 2H-M$^{\mathrm{I}}_{0.1}$YClO and with TAP carbon in 1T-M$^{\mathrm{I}}_{0.2}$YCl$_{0.5}$. These are depicted in Figure 1b,c,d, respectively. The two oxide structures may be formed with all the alkali metals (except 2H-Li$_{0.1}$YClO) and correspond to the placement of the alkali metal in either TAP or trigonal-prismatic (TP) interstices, respectively.[13] In contrast, intercalates of layered transition-metal disulfides generally occur with either TAP and TP coordination only for a single alkali metal.[14] The 3R structure type again represents the direct derivatization of the parent YCl. Depending on conditions, either the 3R or 2H type (and occasionally both) can be obtained with Y$_2$O$_3$ and YCl$_3$ as reactants but only the 3R type when YOCl is used. High concentrations of M$^{\mathrm{I}}$Cl produce only the 3R type, with a clear nonstoichiometry in 3R-K$_x$YClO, $\sim$0.11 < *x* < 0.25, judging from the *c* axis dependence on KCl concentration; this probably occurs with other alkali metals as well. Oxidation of either M$_x$YClO type structure with I$_2$ in CH$_3$CN generates YOCl, the 3R phase yielding a well-crystallized sample in the new YOF type structure (YOCl is normally PbFCl type). The 3R phase reversibly picks up water from moist air to form a probable monohydrate (1T) for at least K and Rb but not Li. Liquid water gives slow oxidation to YOCl together with a striking exfoliation.

The new 1T-ScClC$_{0.5}$ and YClC$_{0.5}$ are isostructural with 1T-TaSC$_{0.5}$ and also occur as intercalates with alkali metals with retention of the 1T form, Figure 1d. (TaSC$_{0.5}$ intercalates evidently occur in other structures.[15]) Both the introduction of carbon into all TAP sites in M′Cl and the intercalation step provide striking reductions in the metal–metal distances within the slabs, i.e., by 0.0793 (5) and 0.131 (8) Å in the intra- and interlayer distances between YCl and K$_{0.26}$YClC$_{0.5}$. The intercalated carbides are readily decomposed by water. More details will be published in full articles.[16]

Interstitial non-metals have also been found within some extended-chain structures that exhibit strong metal–metal bonding[17] and may be quite common. Nonetheless, a good number of other cluster and chain compounds show no X-ray evidence whatsoever for incorporation of any guest impurity atoms.

Supplementary Material Available: A listing of atom and cell parameters for the six indicated compounds (2 pages). Ordering information is given on any current masthead page.

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Articles

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Electrochemical and Spectroscopic Studies of 3,5-Di-*tert*-butylcatecholato and 3,5-Di-*tert*-butyl-*o*-semiquinonato Complexes of Copper(II)

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Reduction of mixtures of copper(II) and 3,5-di-*tert*-butyl-*o*-benzoquinone (DTBQ) at mole ratios of 1:2 in acetonitrile or dimethyl sulfoxide yields a copper(II)–catecholato (DTBC)–semiquinonato (DTBSQ) complex [Cu$^{\mathrm{II}}$(DTBC)(DTBSQ)$^-$] and a Cu$^{\mathrm{II}}$(DTBC)$_2^{2-}$ complex. These complexes, their oxidation products, and three mixed-ligand complexes [Cu$^{\mathrm{II}}$(DTBC)(bpy), Cu$^{\mathrm{II}}$(DTBC)(phen), and Cu$^{\mathrm{II}}$(DTBC)(en)] have been characterized by cyclic voltammetry, optical spectroscopy, and ESR. The formation constants, K_f, for the Cu$^{\mathrm{II}}$(DTBC)(DTBSQ)$^-$ and Cu$^{\mathrm{II}}$(DTBC)$_2^{2-}$ complexes have approximate values of 4×10^{14} and 1.6×10^{33} M^{-2}, respectively. Formation of a stable copper(II)–semiquinonato complex as a redox intermediate provides another versatile 1-electron pathway for the copper–catechol–quinone system, which may be pertinent to the redox chemistry of related systems in biology and to catalytic oxygen activation.

Copper, which is an essential component of many oxidase and oxygenase enzymes,[1-8] appears to be required for lignin formation in plants,[9] and its complexes catalyse oxidative delignification processes.[10] Electrochemical studies indicate

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that the catalytically active copper centers have redox potentials between +0.3 and −0.3 V vs. SCE. Because quinones accelerate the delignification rate,[11] the interaction of their reduction products (semiquinones and catechols) with copper ions may be important to the catalytic process. Such complexes would provide a means to tune the redox potentials and to stabilize intermediate species during the delignification process.

The redox properties of 3,5-di-*tert*-butyl-*o*-benzoquinone (DTBQ), its semiquinone ($DTBSQ^{-}$), and its catechol ($DTBC^{2-}$) in aprotic media have been characterized in a previous paper.[12] The structural and redox chemistry of the semiquinonato and catecholato complexes of iron,[13,14] chromium,[13,15] vanadium,[15-18] manganese,[19] and zinc[20] has been described.

The present paper summarizes the results of an electrochemical and spectroscopic characterization of stable $DTBC^{2-}$ and $DTBSQ^{-}$ complexes of Cu(II) in acetonitrile.

Experimental Section

Equipment. The cyclic voltammetry and controlled-potential electrolyses were accomplished by use of a three-electrode potentiostat (Princeton Applied Research Model 173 potentiostat/galvanostat, Model 175 universal programmer, and Model 179 digital coulometer) and Houston Instrument Model 100 Omnigraphic X-Y recorder.

Electrochemical measurements made use of a Brinkmann electrochemical cell that was equipped with a Beckman platinum-inlay working electrode (area 0.23 cm^2) and a platinum-flag auxiliary electrode (contained in a glass tube with medium-porosity glass frit and filled with a concentrated solution of supporting electrolyte); a Ag/AgCl reference electrode (filled with aqueous tetramethylammonium chloride solution and adjusted to 0.000 V vs. SCE) with a solution junction via a glass tube closed with a cracked-glass bead that was contained in a luggin capillary. Platinum-mesh working and auxiliary electrodes were used for the controlled-potential electrolyses.

The UV–visible spectrophotometric measurements were made with a Cary Model 17D spectrometer, and the EPR spectra were obtained with a Bruker Model ER200D ESR spectrometer.

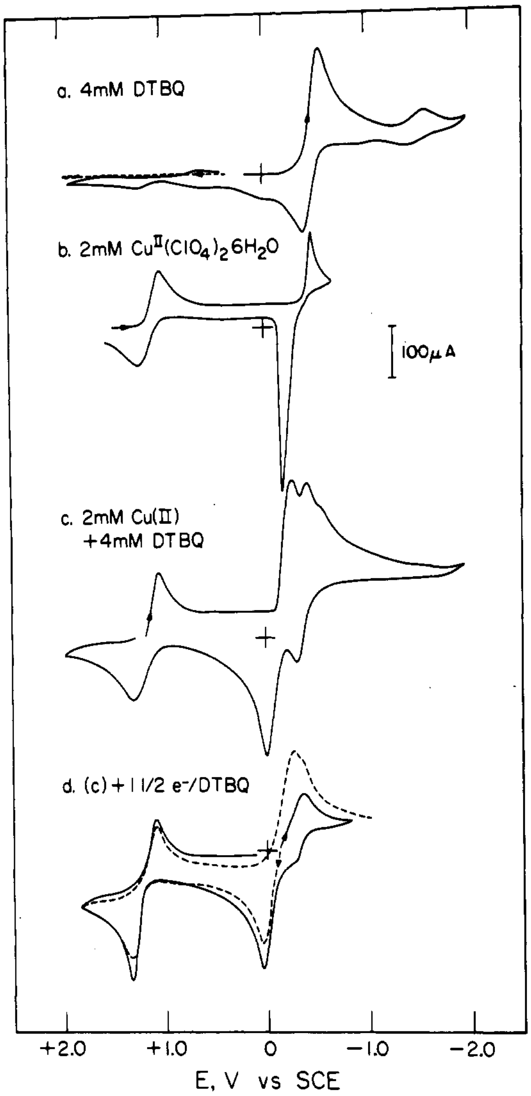

Figure 1. Cyclic voltammograms in MeCN (0.1 M TEAP) of (a) 3,5-di-*tert*-butyl-*o*-quinone (DTBQ), (b) $Cu^{II}(ClO_4)_2 \cdot 6H_2O$, (c) 1:2 combination of $Cu^{II}(ClO_4)_2 \cdot 6H_2O$ and DTBQ, and (d) 1:2 $Cu^{II}(ClO_4)_2 \cdot 6H_2O$–DTBQ after the addition of 1.5 electrons (by reductive electrolysis) per DTBQ (scan rate 0.1 V s^{-1}; Pt electrode (area 0.23 cm^2)).

Reagents. The Cu(II) source was $Cu^{II}(ClO_4)_2 \cdot 6H_2O$ (G. Frederick Smith), dried in vacuo at room temperature. The other reagents, which included 3,5-di-*tert*-butyl-*o*-benzoquinone (DTBQ) (Aldrich), tetraethylammonium perchlorate (TEAP) (G. Frederick Smith), copper(I) chloride (Aldrich) dried in vacuo, and acetonitrile (Burdick and Jackson Laboratories, "distilled in glass"), were used without further purification.

The bis(3,5-di-*tert*-butylcatecholato)copper(II) complex, $Cu^{II}(DTBC)_2^{2-}$, was prepared by a previous method[21] and in situ by the combination of copper(I) chloride with 2 equiv of DTBQ and exhaustive controlled-potential electrolysis at −0.55 V vs. SCE in 50 mL of deaerated supporting electrolyte solution. The electrosynthesized complex, on the basis of UV–visible, electrochemical, and NMR (in Me_2SO-d_6) measurements, was identical with chemically synthesized $Cu^{II}(DTBC)_2^{2-}$. The mixed-ligand complexes, Cu^{II}(DTBC)(bpy), Cu^{II}(DTBC)(phen), and Cu^{II}(DTBC)(en) (where bpy represents bipyridine, phen = 1,10-phenanthroline, and en = ethylenediamine), were prepared by the method of Brown.[22] The purity of these complexes was confirmed by their infrared spectra. Identical species were prepared in situ by the electrochemical reduction at −0.55 V

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Table I. Redox Reactions for Copper–Catechol–Semiquinone–Quinone Systems[a]

A. MeCN (0.1 M TEAP)

$$\mathrm{Cu(II)} + e^- \xrightleftharpoons[+1.20\ \mathrm{V}]{+1.03\ \mathrm{V}} \mathrm{Cu(I)} \tag{1}$$

$$\mathrm{Cu(I)} + e^- \xrightleftharpoons[-0.18\ \mathrm{V}]{-0.45\ \mathrm{V}} \mathrm{Cu^0} \tag{2}$$

$$\mathrm{DTBQ} + e^- \xrightleftharpoons[-0.43\ \mathrm{V}]{-0.53\ \mathrm{V}} \mathrm{DTBSQ^-} \tag{3}$$

$$\mathrm{DTBSQ^-} + e^- \xrightleftharpoons[-1.40\ \mathrm{V}]{-1.50\ \mathrm{V}} \mathrm{DTBC^{2-}} \tag{4}$$

$$\mathrm{Cu(I)} + 2\mathrm{DTBQ} + 2e^- \xrightarrow{-0.25\ \mathrm{V}} [\mathrm{Cu^I(DTBSQ)_2^-} \leftrightarrow \mathrm{Cu^{II}(DTBC)(DTBSQ)^-}] \tag{5}$$

$$\mathrm{Cu^{II}(DTBSQ)(DTBC)^-} + e^- \xrightleftharpoons[-0.30\ \mathrm{V}]{-0.40\ \mathrm{V}} \mathrm{Cu^{II}(DTBC)_2^{2-}} \tag{6}$$

$$\mathrm{Cu^{II}(DTBC)(DTBSQ)^-} \xrightarrow{0.00\ \mathrm{V}} \mathrm{Cu(I)} + 2\mathrm{DTBQ} + 2e^- \tag{7}$$

B. Me_2SO (0.1 M TEAP)

$$\mathrm{Cu(II)} + 2e^- \xrightleftharpoons[+0.18\ \mathrm{V}]{-0.12\ \mathrm{V}} \mathrm{Cu^0} \tag{8}$$

$$\mathrm{Cu^{II}(DTBC)(DTBSQ)^-} + e^- \xrightleftharpoons[-0.27\ \mathrm{V}]{-0.35\ \mathrm{V}} \mathrm{Cu^{II}(DTBC)_2^{2-}} \tag{9}$$

$$\mathrm{Cu^{II}(DTBC)(DTBSQ)^-} \xrightleftharpoons[-0.35\ \mathrm{V}]{-0.08\ \mathrm{V}} \mathrm{Cu^{II}(DTBSQ)^+} + \mathrm{DTBQ} + 2e^- \xrightleftharpoons[+0.26\ \mathrm{V}]{+0.34\ \mathrm{V}} \mathrm{Cu(II)} + 2\mathrm{DTBQ} + 3e^- \tag{10}$$

C. Me_2SO (0.1 M TEAP); Mixed-Ligand (Phenathroline–DTBC) Complex

$$\mathrm{Cu^{II}(DTBC)(phen)} + \mathrm{H_2O} + e^- \xrightleftharpoons[-0.33\ \mathrm{V}]{-1.04\ \mathrm{V}} \mathrm{Cu^I(phen)^+} + \mathrm{DTBCH^-} + \mathrm{OH^-} \tag{11}$$

$$\mathrm{Cu^{II}(DTBC)(phen)} \xrightleftharpoons[-0.04\ \mathrm{V}]{+0.06\ \mathrm{V}} \mathrm{Cu^{II}(phen)^{2+}} + \mathrm{DTBQ} + 2e^- \tag{12}$$

[a] Voltammetric peak potentials are for a platinum electrode (0.1 V s^{-1}) and are vs. SCE.

vs. SCE of 1:1:1 mole ratios of Cu^ICl:DTBQ:L (L = bpy, phen, en). The 3,5-di-*tert*-butyl-*o*-semiquinone anion radical ($DTBSQ^-$) was formed in MeCN and Me_2SO by controlled-potential electrolysis of DTBQ at −0.65 V vs. SCE.

Results

Electrochemistry. Figure 1 illustrates the cyclic voltammograms for acetonitrile solutions of 3,5-di-*tert*-butyl-*o*-quinone (DTBQ), $Cu^{II}(ClO_4)_2·6H_2O$ (Cu(II)), and the 1:2 combination of Cu(II) and DTBQ and its reduction product. The redox reactions for these processes and for similar ones in dimethyl sulfoxide are summarized in Table I. The reduction of DTBQ in the presence of Cu(II) (Figure 1c) occurs at a peak potential 0.31 V more positive than that of a metal-free solution and occurs in two steps. (A small cathodic peak (≃5%) appears at −0.55 V, the height of which is dependent on the residual water content of the solvent.) For the 1:2 Cu(II)–DTBQ combination, a cathodic peak is not observed at −1.50 V, in contrast to the case for free DTBQ (Figure 1a). Also, this combination does not exhibit a sharp anodic peak for the reverse scan, which is observed for free Cu(II) and is due to the oxidation of Cu metal at −0.18 V (Figure 1b). The two cathodic peaks at −0.25 and −0.4 V of Figure 1c yield the anodic peaks at 0.00 and −0.30 V, respectively.

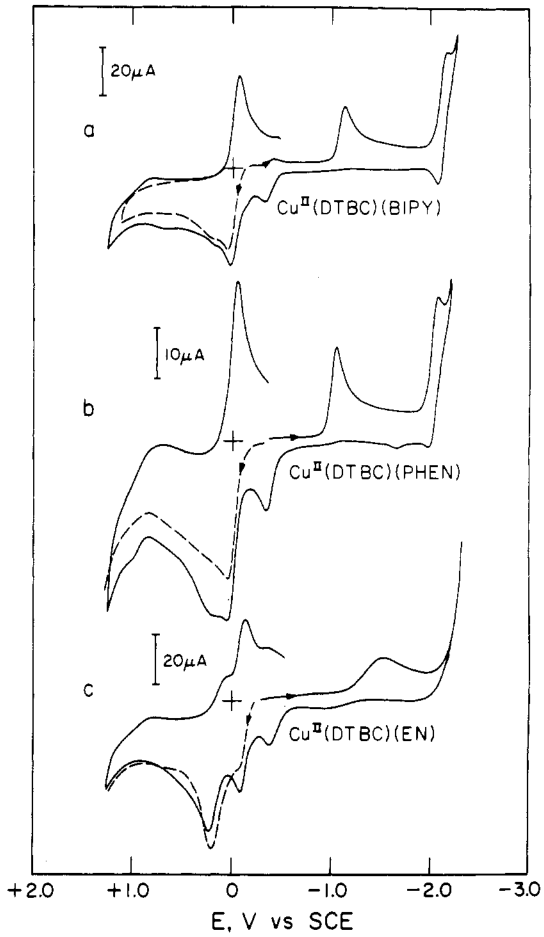

Figure 2. Cyclic voltammograms in Me_2SO (0.1 M TEAP) of (a) 2.0 mM Cu^{II}(DTBC)(bpy), (b) 2.0 mM Cu^{II}(DTBC)(phen), and (c) 2.0 mM Cu^{II}(DTBC)(en) (scan rate 0.1 V s^{-1}; Pt electrode (area 0.23 cm^2)).

The controlled-potential reduction of the 1:2 Cu(II)–DTBQ combination solution at −0.25 V, which requires 1.5 electrons per DTBQ, yields an air-sensitive green solution. The latter exhibits a reduction peak at −0.4 V (Figure 1d) and an oxidation peak at 0.00 V for initial negative and positive scans, respectively.

Controlled-potential reduction of this green solution at −0.4 V requires 0.5 electron per DTBQ to give an extremely air-sensitivie product that is colorless and does not exhibit any cathodic electrochemistry. (Its rest potential is −0.45 V; the voltammogram for an initial positive scan is identical with the reverse scan of Figure 1c).

Controlled-potential oxidation at +0.25 V of the colorless product solution (from reductive electrolysis of a 1:2 Cu(II)–DTBQ coimbination at −0.45 V) requires 1.5 electrons per DTBQ to give a yellow solution. The latter exhibits a cyclic voltammogram that is equivalent to that for the starting solution (after reduction of free Cu(II), Figure 1c).

A 1:1 Cu(II)–DTBQ combination exhibits a cyclic voltammogram that is similar to that of Figure 1c for the 1:2 combination, but it has an additional sharp anodic peak for the reverse scan (analogous to that for the reverse scan after reduction of free Cu(II)).

The cyclic voltammograms of the Cu^{II}(DTBC)(bpy), Cu^{II}(DTBC)(phen), and Cu^{II}(DTBC)(en) complexes in Me_2SO are illustrated in Figure 2. An initial negative scan yields a 1-electron reduction peak at approximately −1.0 V for the Cu^{II}(DTBC)(bpy) and Cu^{II}(DTBC)(phen) complexes and at −1.5 V for the Cu^{II}(DTBC)(en) complex. This reduction peak is coupled to a 1-electron oxidation at approximately −0.3 V (scan reversal after the reduction peak yields an equally intense oxidation peak (Figure 2)). Similar electrochemistry is observed for the first two complexes in CH_3CN and DMF. The $Cu^{II}(DTBC)(bpy)$ and $Cu^{II}(DTBC)(phen)$ systems exhibit a 2-electron oxidation at approximately +0.05 V in all three solvents. The $Cu^{II}(DTBC)(en)$ complex undergoes two 1-electron oxidations in Me_2SO and DMF. Becuase $Cu^{II}(DTBC)(en)$ is insoluble in CH_3CN, meaningful electrochemical data could not be obtained. The redox reactions for the $Cu^{II}(DTBC)(phen)$ complex in Me_2SO, which are representative of this group of mixed-ligand Cu(II) complexes, are summarized in Table IC.

Optical Spectroscopy. The UV–visible spectra of DTBQ, of its semiquinone anion ($DTBSQ^-$), and of 3,5-di-*tert*-butylcatechol ($DTBCH_2$) and its anions have been presented in a previous paper.[12] Figure 3 illustrates the UV–visible spectra for acetonitrile (0.1 M TEAP) solutions of $DTBSQ^-$, $Cu^{II}(DTBC)(DTBSQ)^-$ [prepared by controlled-potential electrolysis at −0.25 V (1 electron per DTBQ) of a 1:2 Cu(I)–DTBQ combination], and $Cu^{II}(DTBC)^{2-}$ [prepared by controlled-potential electrolysis at −0.40 V (1.5 electrons per DTBQ) of a 1:2 Cu(I)–DTBQ combination]. The spectrum of $[Cu^{II}(DTBC)(DTBSQ)^- \leftrightarrow Cu^{I}(DTBSQ)_2^-]$ includes a band at 382 nm (ϵ 5300 M^{-1} cm^{-1}, per total ligand) (Figure 3b) that has approximately two-thirds the intensity as that for free $DTBSQ^-$ (λ_{max} 376 nm, ϵ 7500 M^{-1} cm^{-1}). In the case of $Cu^{II}(DTBC)_2^{2-}$ (Figure 2c), the 382-nm band is almost absent. The spectrum for the oxidation product of $Cu^{II}(DTBC)_2^{2-}$ (oxidized at +0.25 V) is identical with that for free DTBQ. The reduction products for 1:1 combinations of $Cu^{I}Cl$ and DTBQ have spectra that are similar to those for the reduction products of 1:2 combinations.

ESR Spectroscopy. Figure 4 illustrates the ESR spectra at 77 K of $Cu^{II}(ClO_4)_2 \cdot 6H_2O$ and $Cu^{II}(DTBC)_2^{2-}$ (Cu(II) + 2 DTBQ + 2 electrons/DTBQ at −0.4 V) in acetonitrile (0.1 M TEAP). The spectrum for $Cu^{II}(DTBC)_2^{2-}$ [$g_\parallel = 2.24$ (190 G), $g_\perp = 2.05$ (50 G)] is strikingly different from that for $Cu^{II}(ClO_4)_2 \cdot 6H_2O$ [$g_\parallel = 2.41$ (120 G), $g_\perp = 2.08$]. The $Cu^{II}(DTBC)(DTBSQ)^-$ complex (Cu(II) + 2 DTBQ + 1.5 electrons/DTBQ at −0.2 V) is ESR inactive (only a weak signal that corresponds to ca. 5% $Cu^{II}(DTBC)_2^{2-}$ is observed). Oxidation of $Cu^{II}(DTBC)_2^{2-}$ at +0.25 V yields a product solution that is ESR silent.

Discussion and Conclusions

The electrochemical (Figure 1) and spectroscopic data (Figures 3 and 4) indicate that Cu(II) forms stable complexes with $DTBC^{2-}$ and $DTBSQ^-$. The electrochemical redox reactions for $Cu^{II}(ClO_4) \cdot 6H_2O$ (Figure 1b), DTBQ (Figure 1a), and their 1:2 combination (Figure 1c) are summarized in Table I. These are consistent with the controlled-potential electrolysis stoichiometries and the spectroscopic data. A self-consistent reduction sequence for a 1:2 Cu(II)–DTBQ combination in MeCN is represented by reactions 1, 5, and 6 of Table I.

The absorption band at 382 nm in the optical spectrum for the reduction product of reaction 5 (Table I) is consistent with a single $DTBSQ^-$ in the formula of the complex $[Cu^{II}(DTBC)(DTBSQ)^-]$. The absence of an EPR signal for this product species is consistent with antiferromagnetic coupling between Cu(II) and $DTBSQ^-$. The diamagnetism also could be explained by formulation of the product as $Cu^{I}(DTBSQ)_2^-$ with the electron spins of the two semiquonones antiferromagnetically coupled. However, its optical spectrum and electrochemistry support the formulation as $Cu^{II}(DTBC)(DTBSQ)^-$. Furthermore, a broad band due to a d–d transition for Cu(II) appears to be present in the near-IR region of its spectrum (Figure 3).

Electrochemical reduction of the $Cu^{II}(DTBC)(DTBSQ)^-$ complex (reaction 6, Table I) causes the 382-nm band of Figure 3c to disappear and yields an ESR-active product (Figure 4b). The ESR signal corresponds to the interaction of the unpaired electron with the Cu(II) nucleus in axial symmetry and is consistent with formulation of the reduction product as $Cu^{II}(DTBC)_2^{2-}$. The high value of the coupling constant ($A_\parallel = 190$ G) indicates that the unpaired spin density residues mostly in the metal orbitals, as has been observed for the Fe(III) semiquinone complexes.[14]

The small reduction peak at −0.55 V on curve c of Figure 1 probably is due to free DTBQ that is formed from the hydrolysis of $Cu^{II}(DTBC)(DTBSQ)^-$ by water (reduction of this DTBQ yields the original complex).

Oxidation of $Cu^{II}(DTBC)_2^{2-}$ is a two-step process (reverse of reaction 6 plus reaction 7, Table I and Figure 1c); the electron stoichiometry is confirmed by controlled-potential coulometry. The products of reaction 7 (Cu(I) and DTBQ, Table I) are confirmed by the electrochemistry and spectroscopy of the product solution; there is an oxidation peak at +1.3 V for Cu(I) → Cu(II).

Stability Of Complexes. A rough measure of the stability of the copper(II)–DTBC–DTBSQ complexes is provided by the shift in oxidation potentials ($\Delta E_{p/2}$) for the bound $DTBSQ^-$ and $DTBC^{2-}$ groups relative to those for the free ligands. Such an estimate assumes that there is no interaction between DTBQ and Cu(II) or Cu(I). The shift in potential for the oxidation of $DTBSQ^-$ in $[Cu^{II}(DTBC)(DTBSQ)^- \rightleftarrows Cu^{I}(DTBSQ)_2^-]$

$$Cu^{I}(DTBSQ)_2^- \xrightarrow{E_{p,a} = 0.00\ V} Cu(I) + 2DTBQ + 2e^- \quad (13)$$

relative to that for free $DTBSQ^-$

$$DTBSQ^- \xrightarrow{E_{p,a} = -0.43\ V} DTBQ + e^-$$

expressed as $\Delta E_{p,a}$ and roughly equal to the difference in half-peak potentials, $\Delta E_{p/2,a}$, provides a direct measure of the formation constant for $Cu^{I}(DTBSQ)_2^-$

$$\log K_f' = \frac{\Delta E_{p,a}}{0.059/2} = \frac{0.43}{0.0295} = 14.6 \quad (14)$$

where[23]

$$K_f' = \frac{[Cu^{II}(DTBC)(DTBSQ)^- \leftrightarrow Cu^{I}(DTBSQ)_2^-]}{[Cu(I)][DTBSQ^-]^2} = 4 \times 10^{14}$$

This estimate assumes that $Cu^{I}(DTBSQ)_2^-$ is thermodynamically equivalent to $Cu^{II}(DTBC)(DTBSQ)^-$.

Similar arguments yield a basis for the estimation of the formation constant for $Cu^{II}(DTBC)_2^{2-}$, K_f. Thus, the ratio of K_f to K_f' is related to the difference in the peak potential

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[23] This follows from the Nernst expression for the oxidation of free $DTBSQ^-$ and the assumption that, at the half-peak potential, $E_{p/2,a}$, $[DTBQ] = [DTBSQ^-]$ at the electrode surface:

$$(E_{p/2,a})_{simple} = E^\circ_{DTBQ/DTBSQ^-} + \frac{0.059}{1} \log \frac{[DTBQ]}{[DTBSQ^-]}$$

Substitution in this expression for $[DTBSQ^-]$ from the K_f' expression

$$[DTBSQ^-] = \frac{[Cu^{I}(DTBSQ^-)_2^-]^{1/2}}{[Cu(I)]^{1/2} K_f'^{1/2}}$$

gives

$$(E_{p/2,a})_{complex} = E^\circ_{DTBQ/DTBSQ^-} + 0.059 \log \frac{[DTBQ][Cu(I)]^{1/2} K_f'^{1/2}}{[Cu^{I}(DTBSQ)_2^-]^{1/2}}$$

At the half-peak potential, $[Cu(I)] \approx [Cu^{I}(DTBSQ^-)_2^-]$ at the electrode surface. Hence, the difference in half-peak potentials gives a measure of K_f':

$$(E_{p/2,a})_{complex} - (E_{p/2,a})_{simple} = \Delta E_{p/2,a} = \frac{0.059}{2} \log K_f'$$

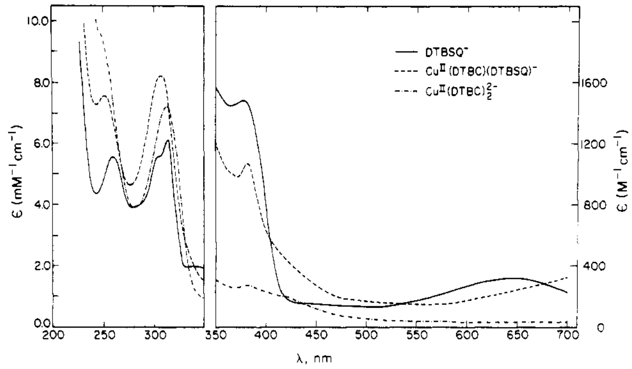

Figure 3. Absorption spectra in MeCN (0.1 M TEAP) for 2.0 mM $DTBSQ^-$, 1 mM $[Cu^{II}(DTBC)(DTBS)^- \leftrightarrow Cu^I(DTBSQ)_2^-]$, and 1.0 mM $Cu^{II}(DTBC)_2^{2-}$. Molar absorptivities are per total ligand concentration.

for the oxidation of bound $DTBC^{2-}$ in $Cu^{II}(DTBC)_2^{2-}$ to bound $DTBSQ^-$ and the peak potential for the oxidation of free $DTBC^{2-}$ to free $DTBSQ^-$[24]

$$0.059 \log \frac{K_f}{K_f'} \simeq \Delta E_{p,a} = \Delta E_{p/2,a} = [-0.30 - (-1.40)] = 1.10 \quad (15)$$

Hence

$$K_f = \frac{[Cu^{II}(DTBC)_2^{2-}]}{[Cu(II)][DTBC^{2-}]^2} = (4 \times 10^{18})K_f' = 1.6 \times 10^{33}$$

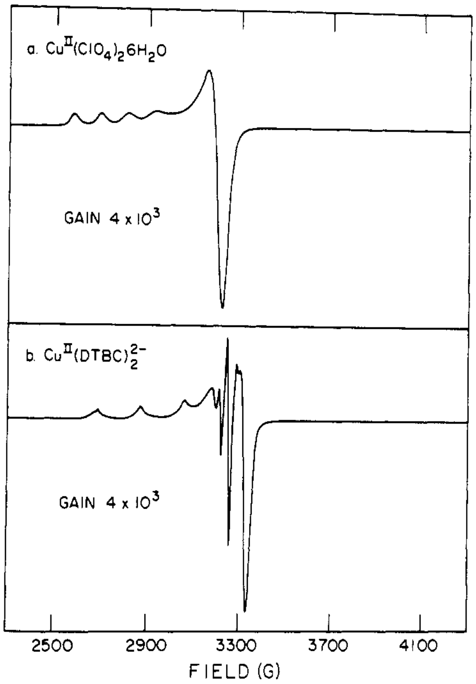

Figure 4. ESR spectra for MeCN solutions of (a) 2 mM $Cu^{II}(ClO_4)_2 \cdot 6H_2O$ and (b) 2 mM $Cu^{II}(DTBC)_2^{2-}$ at 77 K.

Reference to Figure 2 and Table IC indicates that the mixed-ligand complexes, Cu^{II}(DTBC)(phen), Cu^{II}(DTBC)(bpy), and Cu^{II}(DTBC)(en), strongly stabilize the copper(II) state with respect to reduction. In the case of Cu^{II}(DTBC)(phen), the complexed Cu(II) is reduced at −1.04 V vs. SCE to the $Cu^I(phen)^+$ complex, while free solvated Cu(II) is reduced at −0.12 V to metallic copper.

The present study confirms that Cu(II) forms stable $[Cu^{II}(DTBC)_2^{2-}]$ and $[Cu^{II}(DTBC)(DTBSQ)^-]$ complexes in aprotic media and that their electrochemical interconversion is quasi-reversible. The electrochemistry is ligand based, and the copper redox chemistry occurs via electron transfer to and from the ligand.

The interconversion of $Cu^{II}(DTBC)_2^{2-}$ and $Cu^{II}(DTBC)(DTBSQ)^-$ and of Cu^{II}(DTBC)(phen) and $[Cu^{II}(phen)^{2+}$ + DTBQ] in aprotic media resemble certain physiological processes, and the complexes may prove to be effective reaction mimics for superoxide dismutases, oxygen-transfer proteins, and electron-transfer proteins. The formation of stable copper–semiquinone complexes may indicate that stable O_2^- complexes of copper can be formed. Further studies of the reactions of these complexes with superoxide, peroxides, and dioxygen are in progress.

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Registry No. $Cu^{II}(DTBC)(DTBSQ)^-$, 86822-03-9; $Cu^{II}(DTBC)_2^{2-}$, 86822-04-0; Cu^{II}(DTBC)(bpy), 59368-85-3; Cu^{II}(DTBC)(phen), 59368-86-4; Cu^{II}(DTBC)(en), 74463-13-1; DTBQ, 3383-21-9; Cu, 7440-50-8.

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[24] Consideration of the Nernst expressions for oxidation of $Cu^{II}(DTBC)_2^{2-}$ and of $DTBC^{2-}$ and several assumptions yield the relation of eq 15. For the complex

$$(E_{p/2,a})_{complex} = E^{\circ\prime}{}_{DTBSQ^-/DTBC^{2-}} + \frac{0.059}{1} \log \frac{[DTBSQ^-]_c}{[DTBC^{2-}]_c}$$

From

$$K_f'' = \frac{[Cu^{II}(DTBC)(DTBSQ)^-]}{[Cu(II)][DTBC^{2-}][DTBSQ^-]}$$

$$[DTBSQ^-]_c = \frac{[Cu^{II}(DTBC)(DTBSQ)^-]}{K_f'[Cu(II)][DTBC^{2-}]}$$

and from

$$K_f = \frac{[Cu^{II}(DTBC)_2^{2-}]}{[Cu(II)][DTBC^{2-}]^2}$$

$$[DTBC^{2-}]_c = \frac{[Cu^{II}(DTBC)_2^{2-}]}{[Cu(II)][DTBC^{2-}]K_f}$$

Substitution of these quantities into the Nernst expression and the assumptions (a) that at the half-peak potential for the complex $[Cu^{II}(DTBC)(DTBSQ)^-] = [Cu^{II}(DTBC)_2^{2-}]$ at the electrode surface and (b) that at the half-peak potential for the oxidation of free $DTBC^{2-}$ to $DTBSQ^-$ their concentrations at the electrode surface are equal will give

$$(E_{p/2,a})_{DTBC^{2-}} = E^{\circ\prime}{}_{DTBSQ^-/DTBC^{2-}}$$

and yield

$$(E_{p/2,a})_c - (E_{p/2,a})_{DTBC^{2-}} = \Delta E_{p/2,a} = 0.059 \log \frac{K_f}{K_f''}$$

A reasonable estimate is that the formation reactions for $Cu^{II}(DTBC)(DTBSQ)^-$ and $Cu^I(DTBSQ)_2^-$ have equivalent thermodynamics and roughly equal formation constants; $K_f'' \simeq K_f'$. Hence

$$\Delta E_{p/2,a} \simeq 0.059 \log \frac{K_f}{K_f'}$$