orbital studies. Specifically, the total isomer shift values for a series of clusters provides a measure of the relative charge associated with the iron cluster framework. Finally, there is a direct relationship between the isomer shift and the Slater effective nuclear charge experienced by the iron 4s electrons.

Acknowledgment. The authors thank Dr. J. M. Williams of Argonne National Laboratory for a small sample of $HFe_4(CO)_{12}(\eta^2\text{-}CH)$ (VII), which was used in his neutron diffraction studies.[17] It gave results identical with those of the sample prepared at Northwestern University and used in this study. We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for their support of this research. Sample preparation at Northwestern University was supported by the National Science Foundation. We thank Joseph Hriljac for some of the samples and Drs. S. Harris, C. E. Housecroft, T. P. Fehlner, H. Kaesz, and F. Grandjean for many helpful discussions during the course of this work.

Registry No. I, 69665-30-1; II, 80063-51-0; III, 74792-03-3; IV, 77674-97-6; V, 99922-06-2; VI, 72872-04-9; VII, 76547-44-9; VIII, 79061-73-7.

Copper–Catechol Chemistry. Synthesis, Spectroscopy, and Structure of Bis(3,5-di-*tert*-butyl-*o*-semiquinato)copper(II)

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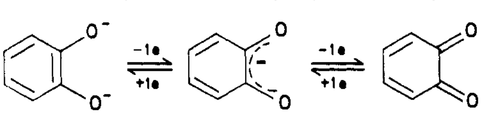
Abstract: The synthesis, spectroscopy, structure, and reactivity of bis(3,5-di-*tert*-butyl-*o*-semiquinato)copper(II), $Cu(DTBSQ)_2$, a Cu(II)–semiquinone complex, are presented. This compound was prepared by reacting $[Cu(pyridine)_4]X$ ($X = ClO_4$, Cl) with the corresponding benzoquinone or a basic Cu(II) dimer, $[Cu_2(pyridine)_4(OCH_3)_2](ClO_4)_2$, with the catechol. The complex, which was characterized by analytical, spectroscopic, and X-ray diffraction techniques, crystallizes in the triclinic space group $P\bar{1}$ with $Z = 2$ in a unit cell of dimensions $a = 10.262$ (3) Å, $b = 14.554$ (4) Å, $c = 9.418$ (2) Å, $\alpha = 101.09$ (2)°, $\beta = 92.31$ (2)°, $\gamma = 108.87$ (2)° at −100 °C. Least-squares refinement of 298 variables led to a value of the conventional R index of 0.049 and $R_w = 0.046$ for 2296 reflections having $I > 3\sigma(I)$. Each copper ion is coordinated to four oxygen atoms from two DTBSQ ligands. In addition, there is a fifth oxygen atom from a neighboring $Cu(DTBSQ)_2$ molecule coordinated to the copper atom in an axial position; thus, the overall geometry about the metal ion approaches square pyramidal. The C–O bond lengths of the DTBSQ ligands range from 1.290 (7) to 1.296 (6) Å. The spectroscopic properties and reactions of $Cu(DTBSQ)_2$ are consistent with the Cu(II)–semiquinone formulation. These results suggest that the copper oxidation of catechols takes place in two one-electron-transfer steps.

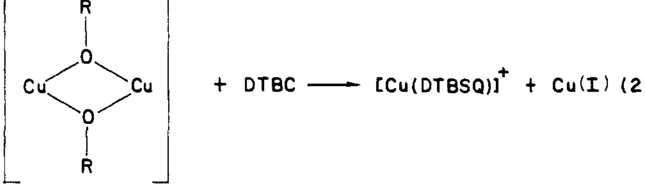
In this contribution, we present the synthesis, spectroscopy, structure, and reactivity of a Cu(II)–3,5-di-*tert*-butyl-*o*-semiquinone (DTBSQ) complex that gives considerable insight into how copper ions oxidize catechols to quinones. This reaction has been of considerable interest for many years because of its synthetic utility and relevance to biological systems.[1-3] The cupric ion clearly functions as an electron acceptor in this oxidation reaction. Dioxygen is used to reoxidize cuprous ion produced during the catalytic reaction but is not necessary for substrate oxidation.[1-3] To date, no copper–catechol species from catalytically active mixtures, which usually consist of cuprous chloride in a pyridine–methanol solvent mixture, have been isolated and characterized, yet several structures have been proposed for the copper-containing intermediates,[1-3] and a simultaneous, two-electron transfer from the catecholate ion to two cupric ions has been suggested as a critical step in the oxidation of catechol to benzoquinone.[1,2]

Our work reported here and elsewhere[4] suggests that this oxidation reaction proceeds in two one-electron-transfer steps with a semiquinone intermediate (eq 1), rather than a single two-electron-transfer step. We recently reported the syntheses and



(1)

structures of a series of Cu(II)–DTBSQ complexes prepared by reacting di-μ-methoxy- or di-μ-hydroxydicopper(II) compounds with the catechol (eq 2) or by reacting Cu(I)–ethylene complexes with the corresponding benzoquinone, DTBBQ (eq 3).[4] Bidentate



(2)

nitrogen-donating ligands are used as the other ligands in the

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(1) Rogic, M. M.; Swerdloff, M. D.; Demmin, T. R. In "Copper Coordination Chemistry: Biochemical and Inorganic Perspectives"; Karlin, K. D., Zubieta, J., Eds.; Adenine Press: New York, 1983; pp 259-279.

(2) (a) Demmin, T. R.; Swerdloff, M. D.; Rogic, M. M. *J. Am. Chem. Soc.* **1981**, *103*, 5795-5804. (b) Rogic, M. M.; Demmin, T. R. *J. Am. Chem. Soc.* **1978**, *100*, 5472-5487. (c) Rogic, M. M.; Demmin, T. R.; Hammond, W. B. *J. Am. Chem. Soc.* **1976**, *98*, 7441-7443. (d) Tsuji, J.; Takayanagi, H. *J. Am. Chem. Soc.* **1974**, *96*, 7349-7350.

(3) (a) Kida, S.; Okawa, H.; Nishida, Y. In "Copper Coordination Chemistry: Biochemical and Inorganic Perspectives"; Karlin, K. D., Zubieta, J., Eds.; Adenine Press: New York, 1983; pp 425-444. (b) Bulkowski, J. E.; Summers, W. E. Reference 3a, pp 445-456. (c) Oishi, N.; Nishida, Y.; Ida, K.; Kida, S. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 2847-2850. (d) Speier, G.; Tyeklar, Z. *J. Molec. Catal.* **1980**, *9*, 233-235.

(4) Thompson, J. S.; Calabrese, J. C. *Inorg. Chem.* **1985**, *24*, 3167-3171.

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copper coordination sphere. The basic Cu(II) dimer–catechol reaction (eq 2) is a critical step in the oxidation of catechol to

$$\mathrm{Cu(I)} + \mathrm{DTBBQ} \rightarrow [\mathrm{Cu(DTBSQ)}]^+ \qquad (3)$$

benzoquinone,[1-3,5] but our work demonstrates for the first time that the semiquinone species is an intermediate in this type of reaction. The Cu(II)–DTBSQ compounds are stable in the absence of compounds such as pyridine and dioxygen. These results are consistent with a recent electrochemical study, which demonstrates the stability of Cu(II)–DTBSQ complexes.[6] The copper coordination chemistry with catechols and benzoquinones thus resembles that of other redox active metal ions, including vanadium, chromium, manganese, iron, cobalt, nickel, and zinc, which all form stable semiquinone complexes. Electrochemical studies of catechols and their complexes established one-electron redox reactions for this species.[7]

This contribution presents a Cu(II)–DTBSQ complex, Cu(DTBSQ)$_2$, prepared under conditions that approximate the first steps in the catalytic reaction, which usually uses cuprous chloride in a pyridine–methanol solvent. Adding dioxygen yields a hydroxy- or methoxy-bridged Cu(II) material, which then reacts with catechol.[1,2] Because our earlier work established that excess pyridine rapidly decomposes the semiquinone complexes to cuprous ion and the corresponding benzoquinone,[4] we have used well-characterized pyridine complexes as the starting material and methanol as the solvent: [Cu(pyridine)$_4$]ClO$_4$, [Cu(pyridine)$_4$]Cl, and [Cu$_2$(pyridine)$_4$(OCH$_3$)$_2$](ClO$_4$)$_2$. These compounds are very similar to those generated in situ during the catalytic reaction.

Experimental Section

General Methods. All chemicals were reagent grade and used as received unless otherwise noted. (Tetrapyridine)copper(I) perchlorate was prepared by a literature procedure.[8] The solvents diethyl ether, dimethylformamide (DMF), methanol, petroleum ether, pyridine, and tetrahydrofuran (THF) were deaerated with prepurified nitrogen and stored over molecular sieves (4 Å), which were treated as described elsewhere.[9] Standard glovebox techniques were used in the handling of air-sensitive compounds. Elemental analyses and molecular weight determination by freezing point depression were performed by Galbraith Laboratories, Inc., Knoxville, TN. Infrared spectra were obtained as Nujol mulls with a Nicolet 5DX Fourier transform infrared spectrophotometer. Electron paramagnetic resonance spectra were obtained on a Bruker ER 200B-SRC spectrometer at −110 °C or room temperature. Absorption spectra were obtained with a Perkin-Elmer 330 spectrophotometer.

Preparation of Bis(3,5-di-*tert*-butyl-*o*-semiquinato)copper(II), Cu(DTBSQ)$_2$. Method A. (Tetrapyridine)copper(I) perchlorate, [Cu(pyridine)$_4$]ClO$_4$ (1.000 g, 2.09 mmol), was dissolved with stirring in 10 mL of methanol. Addition of 3,5-di-*tert*-butyl-*o*-benzoquinone (0.460 g, 2.09 mmol) as a solid gave a dark-green solution, which was stirred for 0.5 h. Removal of solvent under high vacuum yielded a dark-green solid, which was then dissolved in 35 mL of THF. Filtration yielded a green solution and a purple solid. Addition of petroleum ether to the filtrate yielded the dark-green Cu(DTBSQ)$_2$ complex in 95% yield. Anal. Calcd for $C_{28}H_{40}CuO_4$: C, 66.70; H, 8.00. Found: C, 66.43; H, 7.90. IR (cm^{-1}) 1585 s, 1510 s, 1330 w, 1305 m, 1264 m, 1245 s, 1205 w, 1155 w, 1090 s, 1030 m, 990 s, 935 w, 905 m, 870 s, 860 m, 825 m, 805 m, 790 m, 785 w, 750 m, 720 m.

Method B. Addition of dioxygen to [Cu(pyridine)$_4$]ClO$_4$ in methanol followed by diethyl ether yielded [Cu$_2$(pyridine)$_4$(OCH$_3$)$_2$](ClO$_4$)$_2$. Anal. ($C_{22}H_{26}Cl_2CuN_4O_{10}$) C, H, N. IR (cm^{-1}) 1610 s, 1585 w, 1490 m, 1240 w, 1220 m, 1165 w, 1160 m, 1110 s, 1080 s, 1070 s, 1045 s, 1010 w, 995 w, 955 w, 930 w, 865 w, 765 m, 755 m, 705 s, 695 s, 645 w, 640 w, 620 m. This compound (0.660 g, 0.982 mmol) was resuspended in 25 mL of deaerated methanol. 3,5-Di-*tert*-butylcatechol (0.218 g, 0.982 mmol) was added as a solid. The solution was stirred for 0.5 h and then handled as described above.

Table I. Crystal Data for Cu(DTBSQ)$_2$

molecular formula	$C_{28}H_{40}CuO_4$
M_w	504.16
a, Å	10.262 (3)
b, Å	14.554 (4)
c, Å	9.418 (2)
α, deg	101.09 (2)
β, deg	92.31 (2)
γ, deg	108.87 (2)
v, Å^3	1298
Z	2
space group	$P\bar{1}$
radiation	Mo Kα (λ = 0.710 69 Å) from graphite monochromator
2θ limit, deg	4.2–48.0
temp, °C	−100
absorption coeff, cm^{-1}	8.71
transmission factors	0.72–1.13
unique data used (I^2) > $3\sigma(I)$	2296
no. of variables	298
R	0.049
R_w	0.046

Method C. Cuprous chloride (0.500 g, 5.0 mmol) was dissolved in 20 mL of pyridine to yield a bright-yellow solution, which was stirred for 0.5 h. Addition of diethyl ether yielded a yellow precipitate, which was collected by filtration, washed with diethyl ether, and then resuspended in 15 mL of methanol. 3,5-Di-*tert*-butyl-*o*-benzoquinone (1.057 g, 4.8 mmol) was added as a solid to yield a dark-green solution, which was stirred for 0.5 h and handled as described above. Blue solids were removed from the THF solution of the crude product. Removal of THF from the filtrate under high vacuum yielded a green powder in 85% yield, which was washed then with petroleum ether and then recrystallized from THF–petroleum ether at room temperature. Anal. ($C_{28}H_{40}CuO_4$) C, H. IR data are identical with those listed above.

Reactions of Cu(DTBSQ)$_2$. To a THF solution (15 mL) of Cu(DTBSQ)$_2$ (0.125 g, 0.248 mmol) prepared by method A was added triphenylphosphine (0.130 g, 0.496 mmol). A purple solution resulted and was analyzed spectroscopically. Similarly, Cu(DTBSQ)$_2$ (0.125 g, 0.248 mmol) was stirred in a 50/50 mixture of THF and pyridine and was handled in the same manner. Removal of solvent yields a brown solid.

X-ray Data Collection and Structure Solution and Refinement. Crystals suitable for diffraction were obtained by vapor diffusion at room temperature of petroleum ether into a THF solution of Cu(DTBSQ)$_2$ prepared by method A. A black-plate-shaped crystal of dimensions 0.05 × 0.25 × 0.26 mm was handled in the manner described elsewhere,[9] was then placed on a Syntex P3 diffractometer, and was shown to be suitable for diffraction on the basis of ω scans, which showed the peak width at half-height to be ca. 0.29° at −100 °C. The cell parameters were refined on the basis of 17 computer-centered reflections chosen from diverse regions of reciprocal space. These parameters and other crystallographic data are summarized in Table I. Intensity data collection by the ω scan technique, intensity measurements of standard reflections, and data processing were performed as described elsewhere.[9] The solution and refinement of the structure were carried out on an IBM 3081 computer with a system of programs developed by one of us (J.C.C.). The copper atom was located by the heavy-atom Patterson method. The positions of the remaining non-hydrogen atoms were obtained by the usual combination of structure factor and Fourier synthesis calculations and full-matrix least-squares refinement. The function minimized in these refinements is given elsewhere.[9] Atomic scattering factors and anomalous dispersion terms were taken from the usual sources.[10] Hydrogen atom positions were calculated. Least-squares refinement converged to R = 0.049 and R_w = 0.46, where $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$ with w proportional to $1/[\sigma^2(I) + 0.0009I^2]^{1/2}$. All peaks in the final difference map were less than 0.38 e/Å^3 in height.

The final positional parameters for the non-hydrogen atoms appear in Table II. Tables of general temperature factors (Table III), calculated hydrogen atom positions (Table IV), structure factor amplitudes (Table V), and a complete listing of bond distances and angles (Table VI) are available.[11]

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(5) (a) Willett, R. D.; Breneman, G. L. *Inorg. Chem.* **1983**, *22*, 326–329. (b) Gampp, H.; Zuberbuhler, A. D. *Met. Ions Biol. Syst.* **1981**, *12*, 133–189.

(6) Harmalker, S.; Jones, S. E.; Sawyer, D. T. *Inorg. Chem.* **1983**, *22*, 2790–2794.

(7) Pierpont, C. G.; Buchanan, R. M. *Coord. Chem. Rev.* **1981**, *38*, 45–87.

(8) Lewin, A. H.; Michl, R. J.; Ganis, P.; Lepore, U.; Avitabile, G. *J. Chem. Soc., Chem. Commun.* **1971**, 1400–1401.

(9) (a) Thompson, J. S.; Whitney, J. F. *Inorg. Chem.* **1984**, *23*, 2813–2819. (b) Thompson, J. S.; Harlow, R. L.; Whitney, J. F. *J. Am. Chem. Soc.* **1983**, *105*, 3522–3527.

(10) "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV. (a) Table 2.2B. (b) Table 2.31.

(11) See paragraph at end of paper regarding supplementary material.

Table II. Fractional Coordinates (X10 000) for $Cu(DTBSQ)_2$ Parameters

atom	X	Y	Z
Cu(1)	4 121.0 (8)	478.0 (6)	1231.5 (11)
O(1)	2 216 (4)	389 (3)	1257 (5)
O(2)	3 563 (4)	−709 (3)	2053 (4)
O(21)	6 055 (4)	598 (3)	1119 (5)
O(22)	4 806 (4)	1911 (3)	1433 (4)
C(1)	1 533 (6)	−307 (4)	1881 (7)
C(2)	2 288 (6)	−924 (4)	2339 (6)
C(3)	1 596 (6)	−1711 (4)	3016 (6)
C(4)	236 (6)	−1819 (4)	3272 (6)
C(5)	−490 (6)	−1189 (4)	2886 (7)
C(6)	165 (6)	−464 (4)	2174 (7)
C(7)	2 357 (6)	−2372 (5)	3491 (7)
C(8)	3 606 (6)	−1720 (5)	4608 (7)
C(9)	2 853 (7)	−2892 (5)	2158 (8)
C(10)	1 427 (6)	−3159 (5)	4204 (7)
C(11)	−1 989 (6)	−1379 (4)	3251 (7)
C(12)	−2 191 (7)	−1718 (7)	4681 (9)
C(13)	−2 958 (7)	−2186 (7)	2071 (9)
C(14)	−2 354 (8)	−451 (6)	3411 (11)
C(21)	6 830 (6)	1520 (4)	1356 (7)
C(22)	6 149 (6)	2260 (4)	1584 (6)
C(23)	6 943 (6)	3299 (4)	1962 (6)
C(24)	8 352 (6)	3538 (4)	1986 (6)
C(25)	9 053 (6)	2820 (4)	1679 (6)
C(26)	8 302 (6)	1834 (4)	1393 (7)
C(27)	6 240 (6)	4076 (4)	2328 (7)
C(28)	5 349 (6)	3871 (5)	3591 (7)
C(29)	5 314 (6)	4046 (5)	991 (7)
C(30)	7 282 (7)	5128 (5)	2813 (8)
C(31)	10 637 (6)	3212 (4)	1711 (7)
C(32)	11 010 (6)	3794 (5)	490 (8)
C(33)	11 307 (6)	3911 (5)	3194 (7)
C(34)	11 244 (6)	2371 (5)	1486 (7)

Results

Synthesis and Properties. The preparative methods for $Cu(DTBSQ)_2$ are straightforward and are presented in eq 4–6. These reactions involve the one-electron reduction of DTBBQ (eq 4 and 6) or the one-electron oxidation of the catechol (eq 5) and are

$$2[Cu(pyridine)_4]ClO_4 + 2DTBQ \rightarrow Cu(DTBSQ)_2 + [Cu(pyridine)_4](ClO_4)_2 \quad (4)$$

$$4[Cu(pyridine)_4]ClO_4 \xrightarrow[MeOH]{O_2} 2[Cu_2(pyridine)_4(OCH_3)_2](ClO_4)_2 \xrightarrow{DTBC} Cu(DTBSQ)_2 + 2[Cu(pyridine)_x]ClO_4 + [Cu(pyridine)_x](ClO_4)_2 \quad (5)$$

$$2CuCl + pyridine \rightarrow 2[Cu(pyridine)_4]Cl \xrightarrow{DTBBQ} Cu(DTBSQ) + [Cu(pyridine)_4]Cl_2 \quad (6)$$

analogous to the procedure used previously to prepare Cu(II)–DTBSQ complexes with chelating bidentate nitrogen-donating ligands.[4] The initial complex formed is presumably $[Cu(pyridine)_2(DTBSQ)]ClO_4$, analogous to the Cu(II)–DTBSQ complex with 2,2′-dipyridylamine,[4] but this pyridine complex is not isolated; rather, the above reaction with the perchlorate salt yields $Cu(DTBSQ)_2$ and a purple Cu(II) complex, which contains pyridine and gives rise to an EPR spectrum characteristic of a mononuclear Cu(II) complex. This same product is obtained on dissolving $Cu(ClO_4)_2{\cdot}6H_2O$ in pyridine. Recrystallization of this sample from DMF–diethyl ether produces $[Cu(pyridine)_4(DMF)](ClO_4)_2$ in 94% yield, based on analytical and spectroscopic data.[12] The Cu(I)–DTBBQ reaction is the easier of the two procedures.

These preparative procedures yield a dark-green crystalline material, which has physical and spectroscopic properties of a Cu(II)–DTBSQ complex.[4] The compound is stable under an inert atmosphere and gives excellent elemental analyses for the indicated formulation. Cryoscopic molecular weight determination in benzene indicates the presence of only the monomer in solution. Exposure of THF solutions to dioxygen slowly yields DTBBQ, as evidenced by the increased absorption at 400 nm.[3c] Adding methanol hastens the decomposition reaction. No copper products from this reaction have yet been characterized.

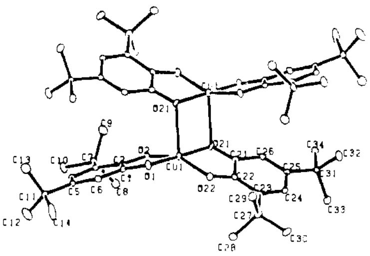

Figure 1. View of the $Cu(DTBSQ)_2$ dimer. The vibrational ellipsoids are drawn at the 50% level. Hydrogen atoms are not shown.

Table VII. Selected Bond Distances (Å) and Angles (deg) for $Cu(DTBSQ)_2$

Cu(1)–O(1)	1.918 (4)	C(3)–C(4)	1.390 (7)
Cu(1)–O(2)	1.955 (4)	C(3)–C(7)	1.536 (8)
Cu(1)–O(21)a	2.416 (4)	C(4)–C(5)	1.440 (8)
Cu(1)–O(21)	1.944 (4)	C(5)–C(6)	1.364 (8)
Cu(1)–O(22)	1.941 (4)	C(5)–C(11)	1.538 (8)
O(1)–C(1)	1.291 (7)	C(7)–C(8)	1.539 (8)
O(2)–C(2)	1.296 (6)	C(7)–C(9)	1.531 (9)
O(21)–C(21)	1.290 (7)	C(7)–C(10)	1.521 (8)
O(22)–C(22)	1.296 (6)	C(11)–C(12)	1.520 (9)
C(1)–C(2)	1.470 (8)	C(11)–C(13)	1.502 (9)
C(1)–C(6)	1.396 (7)	C(11)–C(14)	1.497 (9)
C(2)–C(3)	1.420 (8)		
O(1)–Cu(1)–O(2)	84.9 (2)	C(2)–C(1)–C(6)	120.2 (5)
O(1)–Cu(1)–O(21)a	98.9 (2)	C(1)–C(2)–C(3)	119.6 (5)
O(1)–Cu(1)–O(21)	177.1 (2)	C(2)–C(3)–C(4)	116.7 (5)
O(1)–Cu(1)–O(22)	94.4 (2)	C(2)–C(3)–C(7)	120.6 (5)
O(2)–Cu(1)–O(21)a	88.1 (2)	C(4)–C(3)–C(7)	122.6 (5)
O(2)–Cu(1)–O(21)	97.6 (2)	C(3)–C(4)–C(5)	123.9 (6)
O(2)–Cu(1)–O(22)	151.8 (2)	C(4)–C(5)–C(6)	118.8 (5)
O(21)–Cu(1)–O(21)a	79.7 (2)	C(4)–C(5)–C(11)	118.7 (5)
O(21)a–Cu(1)–O(22)	119.7 (2)	C(6)–C(5)–C(11)	122.5 (5)
O(21)–Cu(1)–O(22)	84.2 (2)	C(1)–C(6)–C(5)	120.7 (5)
Cu(1)–O(21)–Cu(1)a	100.3 (2)	C(3)–C(7)–C(8)	109.1 (5)
Cu(1)–O(1)–C(1)	111.6 (4)	C(3)–C(7)–C(9)	109.3 (5)
Cu(1)–O(2)–C(2)	110.6 (3)	C(3)–C(7)–C(10)	111.8 (5)
Cu(1)a–O(21)–C(21)	119.8 (4)	C(8)–C(7)–C(9)	109.9 (5)
Cu(1)–O(21)–C(21)	110.7 (3)	C(8)–C(7)–C(10)	107.9 (5)
Cu(1)–O(22)–C(22)	111.5 (3)	C(9)–C(7)–C(10)	108.7 (5)
O(1)–C(1)–C(2)	116.6 (5)	C(5)–C(11)–C(12)	111.2 (5)
O(1)–C(1)–C(6)	123.2 (5)	C(5)–C(11)–C(13)	109.3 (5)
O(2)–C(2)–C(1)	115.9 (5)	C(5)–C(11)–C(14)	111.0 (5)
O(2)–C(2)–C(3)	124.4 (5)	C(12)–C(11)–C(13)	108.0 (6)
O(21)–C(21)–C(22)	117.4 (5)	C(12)–C(11)–C(14)	107.1 (6)
O(21)–C(21)–C(26)	123.2 (5)	C(13)–C(11)–C(14)	110.2 (7)
O(22)–C(22)–C(21)	115.4 (5)		
O(22)–C(22)–C(23)	123.9 (5)		

Description of the Structure of $Cu(DTBSQ)_2$. The overall structure of this compound is apparent in the drawing of the molecule (Figure 1) and consists of $Cu(DTBSQ)_2$ dimers. Each copper ion is coordinated to four oxygen atoms from two DTBSQ ligands in a geometry that is distorted from a planar arrangement toward a tetrahedral one. The dihedral angle of the ligand planes (Cu, O1, O2 and Cu, O21, O22) is 28.55°. In addition, there is a fifth oxygen atom from a neighboring $Cu(DTBSQ)_2$ molecule coordinated in an axial position to form a dimer about the crystallographic inversion center; thus, the geometry about the cupric ion approaches a square-pyramidal one. This type of dimerization of planar Cu(II) complexes is very common in copper coordination chemistry.[14]

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(12) (a) Anal. Calcd for $C_{23}H_{27}Cl_2CuN_5O_9$: C, 42.37; H, 4.17; N, 10.74. Found: C, 42.64; H, 4.39; N, 10.71. (b) The EPR spectrum of this material in DMF at −110 °C is very similar to that of $[Cu(N(pyridyl)_3)_2(CH_3CN)_2](CF_3SO_3)_2$, in which the cupric ion is coordinated to four pyridine nitrogen atoms in a planar arrangement and acetonitrile molecules in the axial positions.[13]

(13) Dedert, P. L.; Thompson, J. S.; Ibers, J. A.; Marks, T. J. *Inorg. Chem.* **1982**, *21*, 969–977.

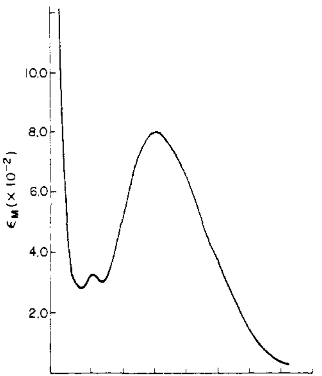

Figure 2. Visible absorption spectrum of $Cu(DTBSQ)_2$ in tetrahydrofuran.

Selected bond distances and angles are presented in Table VII. The observed bond distances and angles for the DTBSQ groups are nearly identical, and the values for only one group are tabulated here.[11] These values are similar to those observed for the DTBSQ group of $[Cu(NHpy_2)(DTBSQ)]ClO_4$ reported elsewhere.[4] The four shorter Cu–O bond lengths are typical of Cu(II)–oxygen distances in general[15] and of a Cu(II)–DTBSQ complex in particular (1.93–1.96 Å).[4] The Cu–O bond length between molecules (2.416 (4) Å) is shorter than that usually observed (2.44–2.66 Å) but is not unique. The C–O distances (1.290 (7)–1.296 (6) Å) are characteristic of DTBSQ complexes, for which the average bond distance is 1.29 Å.[7] Values of 1.284 (8)–1.30 (7) Å were observed for $[Cu(NHpy_2)(DTBSQ)]ClO_4$. The Cu–O and C–O bond lengths as well as the overall geometry of the complex are thus consistent with the formulation of this complex as a Cu(II)–bis(semiquinone) complex.

Spectroscopy. The spectral properties of $Cu(DTBSQ)_2$ are consistent with the formulation of this compound as a Cu(II)–DTBSQ complex. THF solutions are dark green and give rise to the absorption spectrum shown in Figure 2, which is dominated by a broad band centered at 713 nm ($\epsilon = 800\ m^{-1}\ cm^{-1}$). The $[CuL(DTBSQ)]ClO_4$ complexes reported elsewhere[4] give rise to similar spectra (absorption maxima between 825 and 770 nm with $\epsilon = 300\text{–}700\ m^{-1}\ cm^{-1}$). These features are also similar to $[Cu(DTBC)(DTBSQ)]^-$ prepared electrochemically, $DTBSQ^-$, and $Zn(DTBSQ)_2$.[6,16] This band is a ligand band; $Cu(DTBC)_2^{2-}$ has no intense absorption bands in this region.

The X-band EPR spectra of $Cu(DTBSQ)_2$ are consistent with the indicated formulation for this complex.[11] The cupric ion and each of the ligands have an unpaired electron; the complex thus consists of a paramagnetic metal ion coordinated to two paramagnetic ligands. The frozen solution spectrum consists of a broad resonance centered at $g = 2.08$ and a weak, broad (~900 G) feature at $g = 4.34$; no hyperfine structure is observed. In addition, there is a sharp feature at $g = 2.04$. The two broad resonances are characteristic of weakly coupled Cu(II) dimers and may result from the interaction of the unpaired electron on the cupric ion with that on the DTBSQ rings. Transition metal–semiquinone complexes often show strong coupling of spins;[7,17] tris(semiquinone)vanadium(III) complexes have a $S = {}^1/_2$ spin state, resulting from the strong coupling of the d^2 metal ion with two of the ligands and localization of the remaining unpaired electron on the third semiquinone ligand. The broadness of the spectrum for $Cu(DTBSQ)_2$ clearly shows that this type of strong interaction is not present here. However, studies of Cu(II) complexes with paramagnetic ligands have shown interactions varying from very small to very large (estimated $|2J| > 450\ cm^{-1}$).[18,19] Cu(II) superoxide complexes and $[Cu(NHpy_2)(DTBSQ)]ClO_4$ are EPR silent, whereas $Cu(DTBSQ)_2$ as well as some Cu(II)–nitroxyl radical complexes show weaker coupling of spins.[18]

The EPR spectrum of the crystalline solid at −110 °C is considerably different from that in frozen solution and consists of a single, sharp resonance at $g = 2.00$.[11] These different spectral features arise from the different structures in the solid state and solution. The $Cu(DTBSQ)_2$ molecules exist as dimers in the solid state, as shown in the crystal structure determination, and as monomers in solution, as shown by the solution molecular weight determination. The spectral features of the solid-state spectrum suggest strong coupling of the spins of the cupric ions; the sharp resonance at $g = 2.00$ arises from the unpaired spin on the DTBSQ ligand. This type of spectrum has been observed with semiquinone complexes of other paramagnetic metal ions.[7,20]

Reactivity. The reactions of $Cu(DTBSQ)_2$ are consistent with the formulation of this complex as a Cu(II)–semiquinone complex. Adding pyridine to a THF solution of $Cu(DTBSQ)_2$ yields DTBBQ, resulting from an electron transfer from the ligand to the copper ion. A Cu(I)–DTBSQ complex might be expected to result, but instead a Cu(II)–catecholate complex is the only product observed in the EPR spectrum of this solution, which is identical with that of the complex prepared directly. These results are consistent with previous work, which shows that Cu(II)–catecholate complexes are obtained with nitrogen-donating ligands.[21] A Cu(I)–DTBSQ complex is obtained by adding 2 equiv of triphenylphosphine; DTBBQ is also produced. The EPR spectrum of this cuprous complex at room temperature is identical with that reported for the complex prepared directly.[22]

Discussion

The $Cu(DTBSQ)_2$ complex reported here clearly establishes the stability of Cu(II)–semiquinone complexes, which are shown to be indefinitely stable to further oxidation of the DTBSQ ligand under an inert atmosphere and in the absence of molecules such as pyridine. These results suggest that catechol oxidation by basic Cu(II) complexes proceeds in one-electron-transfer steps. The synthetic procedure described above (eq 5) approximates the conditions used for the copper-catalyzed oxidation of catechols to the corresponding benzoquinones.[1-3] The major difference is

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(14) (a) Cotton, F. A.; Wilkinson, G. "Advanced Inorganic Chemistry", 4th ed.; Wiley: New York, 1980; pp 811–818. (b) Garland, M. T.; LeMarouille, J. Y.; Spodine, E. *Acta Crystallogr., Sect. C* **1985**, *C41*, 855–858. (c) Wells, A. F. "Structural Inorganic Chemistry", 4th ed.; Clarendon Press: Oxford, 1975; pp 901–905. (d) Baker, R. T.; Rettig, S. J.; Storr, A.; Trotter, J. *Can. J. Chem.* **1976**, *54*, 343–354.

(15) (a) Gazo, J.; Bersuker, I. B.; Garaj, J.; Kabesova, M.; Kohout, J.; Langfelderova, H.; Melnik, M.; Serator, M.; Valach, F. *Coord. Chem. Rev.* **1976**, *19*, 253–297. (b) Fawcett, T. G.; Ushay, M.; Rose, J. P.; Lalancette, R. A.; Potenza, J. A.; Schugar, H. J. *Inorg. Chem.* **1979**, *18*, 327–332. (c) Foley, J.; Kennefick, D.; Phelan, D.; Tyagi, S.; Hathaway, B. *J. Chem. Soc., Dalton Trans.* **1983**, 2333–2338. (d) Freeman, H. C. *Adv. Protein Chem.* **1967**, *22*, 257–424.

(16) Bodini, M. E.; Copia, G.; Robinson, R.; Sawyer, D. T. *Inorg. Chem.* **1983**, *22*, 126–129.

(17) (a) Cass, M. E.; Greene, D. L.; Buchanan, R. M.; Pierpont, C. G. *J. Am. Chem. Soc.* **1983**, *105*, 2680–2686. (b) Tuchagues, J. M.; Hendrickson, D. N. *Inorg. Chem.* **1983**, *22*, 2545–2552. (c) Buchanan, R. M.; Claflin, J.; Pierpont, C. G. *Inorg. Chem.* **1983**, *22*, 2552–2556. (d) Sofen, S. R.; Ware, D. C.; Cooper, S. R.; Raymond, K. N. *Inorg. Chem.* **1979**, *18*, 234–239. (e) Buchanan, R. M.; Pierpont, C. G. *J. Am. Chem. Soc.* **1980**, *102*, 4951–4957. (f) Buchanan, R. M.; Kessel, S. L.; Downs, H. H.; Pierpont, C. G.; Hendrickson, D. N. *J. Am. Chem. Soc.* **1978**, *100*, 7894–7900. (g) Buchanan, R. M.; Downs, H. H.; Shorthill, W. B.; Pierpont, C. G.; Kessel, S. L.; Hendrickson, D. N. *J. Am. Chem. Soc.* **1978**, *100*, 4318–4320. (h) Wicklund, P. A.; Beckmann, L. S.; Brown, D. G. *Inorg. Chem.* **1976**, *15*, 1996–1997.

(18) (a) Bencini, A.; Benelli, C.; Gatteschi, D.; Zanchini, C. *J. Am. Chem. Soc.* **1984**, *106*, 5813–5818. (b) Dickman, M. H.; Doedens, R. J. *Inorg. Chem.* **1981**, *20*, 2677–2681. (c) Anderson, O. P.; Kuechler, T. C. *Inorg. Chem.* **1980**, *19*, 1417–1422. (d) Eaton, S. S.; Eaton, G. R. *Coord. Chem. Rev.* **1978**, *26*, 207–262.

(19) (a) Thompson, J. S. *J. Am. Chem. Soc.* **1984**, *106*, 4057–4059. (b) Nappa, M.; Valentine, J. S.; Miksztal, A. R.; Schugar, H. J.; Isied, S. S. *J. Am. Chem. Soc.* **1979**, *101*, 7744–7746.

(20) Additional EPR and variable-temperature magnetic susceptibility experiments are in progress and should lead to a clearer understanding of the spectra described here. Results will be presented elsewhere.

(21) (a) Brown, D. G.; Reinprecht, J. T.; Vogel, G. C. *Inorg. Nucl. Chem. Lett.* **1976**, *12*, 399–404. (b) Brown, D. G.; Hughes, W. J. *Z. Naturforsch.* **1979**, *34b*, 1408–1412. (c) Brown, D. G.; Hughes, W. J.; Knerr, G. *Inorg. Chim. Acta* **1980**, *46*, 123–126.

(22) Razuvaev, G. A.; Cherkasov, V. K.; Abakumov, G. A. *J. Organomet. Chem.* **1978**, *160*, 361–371.

the lack of an excess of ligands such as pyridine, which displace DTBBQ from the complex as we have shown here and elsewhere.[4] Adding dioxygen to $[Cu(pyridine)_4]ClO_4$ yields $[Cu_2(pyridine)_4(OCH_3)_2](ClO_4)_2$, a di-$\mu$-methoxy-bridged Cu(II) dimer. This type of complex was suggested as the oxidizing agent in the catalytic reaction.[2,5] Addition of the catechol to the dimer yields a Cu(II)–DTBSQ complex and $[Cu(pyridine)_x]ClO_4$, corresponding to a one-electron oxidation of the catechol. Importantly, the simultaneous two-electron transfer to yield DTBBQ and 2 equiv of Cu(I) ion is not observed, although this reaction has been suggested in the literature.[1-3] These results are consistent with the well-established redox properties of catechol complexes, which undergo one-electron-transfer reactions.

The copper coordination chemistry with DTBSQ ligands is similar to that of other first-row transition metals in terms of synthetic procedures and properties of the complexes.[7] In addition to the procedure described above, the Cu(II)–DTBSQ complex can be prepared from $[Cu(pyridine)_4]X$ ($X = ClO_4$, Cl) and DTBBQ. In this case, the cuprous ion reduces the ligand by one electron to yield Cu(II) ion and DTBSQ. This procedure is analogous to that for other redox active metals, in which metal carbonyls are used as starting materials, and for $[CuL(DTBSQ)]^+$ (L = bidentate nitrogen-donating ligands), in which Cu(I)–ethylene complexes are used.[4] The Cu(II)–DTBSQ complex is also similar to those with Mn(II), Ni(II), Co(II), and Zn(II) ions, in that bis complexes are formed, although in these other cases oligomeric products are obtained.[7]

The structural characterization of $Cu(DTBSQ)_2$ establishes this compound unambiguously as a Cu(II)–*o*-semiquinone complex. The carbon–oxygen bond lengths of the catechol-like ligands indicate the oxidation state of the ligand. The DTBSQ ligand generally has C–O bond lengths of 1.28–1.30 Å. The values observed here fall in this range. Catechols and benzoquinones have bond lengths that are considerably longer (1.36 Å) or shorter (1.23 Å).[7] In addition, the copper coordination sphere observed for $Cu(DTBSQ)_2$ is characteristic of Cu(II) compounds in terms of Cu–O bond lengths and the overall geometry. The dimerization of $Cu(DTBSQ)_2$ moieties observed here is common for copper coordination compounds,[14,15] although the Cu–O bond length with the neighboring molecule is shorter than that typically observed.

The reactions of $Cu(DTBSQ)_2$ indicate the presence of a redox active species. Extensive electrochemical and reactivity studies of semiquinone complexes have shown that this ligand undergoes one-electron oxidations and reductions.[7] Similar reactions are observed here. Adding triphenylphosphine yields benzoquinone and a Cu(I)–DTBSQ complex, the EPR spectrum of which is identical with that previously reported for the Cu(I) complex $Cu(DTBSQ)(P(C_6H_5)_3)_2$.[22] In this reaction, the Cu(II) ion is reduced by a DTBSQ ligand. A similar reaction is observed with added pyridine. DTBBQ is produced, as evidenced by the increased absorption in the visible spectrum at 400 nm. Unlike the phosphine reaction, however, the remaining DTBSQ ligand becomes the electron acceptor to produce a Cu(II)–catecholate complex. The EPR spectrum of this complex is characteristic of a Cu(II) compound and identical with that for the complex prepared directly. These results are consistent with previously reported chemistry that established a ligand dependence for the observation of a Cu(II)–DTBC complex or a Cu(I)–DTBSQ complex. Nitrogen ligands favor the former, whereas phosphine ligands favor the latter.

Conclusion

This work establishes that the oxidation of catechols by basic cupric complexes takes place in one-electron-transfer steps. The starting Cu(II) complexes used in this study are very similar to those suggested as important in the catalytic reaction, which can be viewed as two one-electron-transfer reactions. Catecholate ions are oxidized by cupric ion to produce 1 equiv of cuprous ion and a Cu(II)–SQ complex. In the presence of ligands such as pyridine, the second electron transfer takes place to yield benzoquinone and cuprous ion. The second electron-transfer reaction can thus be thought of in terms of the relative stabilities of the Cu(I) and Cu(II) oxidation states, a feature important in copper coordination chemistry and one that depends strongly on the other ligands present. The solvent systems used for the copper-catalyzed catechol oxidation reactions have in common ligands that stabilize the Cu(I) oxidation state and are thus capable of forcing the second electron transfer to produce benzoquinone and cuprous ion.

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Supplementary Material Available: Listings of general temperature factors (Table III), calculated hydrogen atom positions (Table IV), structure factor amplitudes (Table V), and a complete listing of bond distances and angles (Table VI) and EPR spectra of solution and crystalline samples (11 pages). Ordering information is given on any current masthead page.