also present in SnPc$_2$[19] and UPc$_2$[20] where clearly no phthalocyanine ring is in an oxidized form.

**Registry No.** **1**, 97633-44-8; **2**, 97633-46-0; 1,2-dicyanobenzene, 91-15-6; 1,8-diazabicyclo[5.4.0]undec-7-ene, 6674-22-2.

**Supplementary Material Available:** Listings of thermal and positional parameters and esd's (Tables VII and VIII for LuPc$_2$·CH$_2$Cl$_2$ (**1**) and Tables IX and X for [LuPc(OAc)(H$_2$O)$_2$]·H$_2$O·2CH$_3$OH (**2**)), bond distances and angles (Tables XI and XII for **1** and Tables XIII and XIV for **2**), least-squares planes (Table XV for **1** and Table XVI for **2**), and observed and calculated structure factor amplitudes (Table XVII for **1** and Table XVIII for **2** ($F_o$ and $F_c$, ×10)) and a stereopair of the surroundings of the CCl$_2$ moiety in LuPc$_2$·CH$_2$Cl$_2$, showing one complete and three half LuPc$_2$ molecules (hydrogen atoms omitted) (63 pages). Ordering information is given on any current masthead page.

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Contribution No. 3633 from the Central Research and Development Department,
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# Synthesis, Spectroscopy, and Structures of Copper(II)–3,5-Di-*tert*-butyl-*o*-semiquinone Complexes

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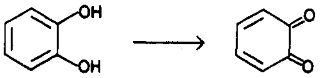
The synthesis, spectroscopy, structures, and reactivity of a series of Cu(II)–di-*tert*-butyl-*o*-semiquinone (DTBSQ) complexes are presented. These compounds were prepared by reacting Cu(I)–ethylene complexes with the corresponding *o*-benzoquinone or by reacting Cu(II) dimers with the catechol. The oxidation states for the metal ion and ligand were assigned from analytical and spectroscopic data. In addition, the di-2-pyridylamine (NH(py)$_2$) complex [Cu(NH(py)$_2$)(DTBSQ)]ClO$_4$·0.5tetrahydrofuran was characterized by X-ray diffraction techniques. The complex crystallizes in the triclinic space group $P\bar{1}$ with $Z = 4$ in a unit cell of dimensions $a = 14.794$ (4) Å, $b = 19.513$ (4) Å, $c = 9.766$ (2) Å, $\alpha = 90.74$ (2)°, $\beta = 105.37$ (2)°, and $\gamma = 93.79$ (2)° at −100 °C. Least-squares refinement of 697 variables led to a value of the conventional $R$ index (on $F$) of 0.050 and $R_w$ of 0.044 for 4107 reflections having $I > 2\sigma(I)$. Each copper ion is coordinated to two pyridyl nitrogen atoms from NH(py)$_2$ and to two oxygen atoms from the DTBSQ ligand. There are two cations in the asymmetric unit with slightly different bond angles and distances about each copper ion. In addition to the NH(py)$_2$ and DTBSQ ligands, the perchlorate anions are coordinated in the axial positions to form distorted-octahedral geometries about each copper ion, with long and short Cu–O interactions. The C–O bond lengths of the coordinated DTBSQ ligand (1.284 (8)–1.304 (7) Å) are characteristic of DTBSQ complexes.

In this contribution, we present the synthesis, spectroscopy, structures and reactivities of a series of Cu(II)–3,5-di-*tert*-butyl-*o*-semiquinone (DTBSQ) complexes prepared by reacting bis($\mu$-methoxy)- or bis($\mu$-hydroxy)dicopper(II) compounds with the catechol or by reacting Cu(I)–ethylene complexes[1,2] with the corresponding *o*-benzoquinone. A series of bidentate nitrogen-donating ligands, with the type of coordinated nitrogen varying from tertiary amines to heterocyclic nitrogen donors, is used as the other ligands in the copper coordination sphere. These ligands allow isolation and complete characterization of the starting materials for both of these synthetic procedures.[1,2] The Cu(II)-dimer–catechol reaction has been suggested as a critical step in the copper-catalyzed oxidation of catechols to quinones (eq 1).[3,4]


(1)

Copper–catechol derivatives from this reaction have not been previously characterized, although several structures have been proposed.[3-5] Our preparative methods are similar to those of *o*-semiquinone complexes with other redox-active metals, including vanadium, chromium, manganese, iron, nickel, and zinc.[6] The metal ions are the electron acceptors for reactions with catechols or electron donors for reactions with quinones, yielding in both cases metal ion–semiquinone complexes. Our results are also consistent with a recent electrochemical study, which demonstrates the stability of Cu(II)–DTBSQ complexes.[7]

## Experimental Section

**General Methods.** All chemicals were reagent grade and used as received unless otherwise noted. The Cu(I)–ethylene complexes were prepared as described elsewhere.[1,2] The solvents methanol, pyridine, diethyl ether, petroleum ether, and tetrahydrofuran (THF) were deaerated with prepurified nitrogen and stored over molecular sieves (4A), which were treated as described elsewhere.[1,2,8] Standard glovebox and Schlenkware techniques were used in the handling of air-sensitive compounds. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN. Infrared spectra were obtained as Nujol mulls with a Perkin-Elmer 283-B infrared spectrophotometer. NMR spectra were obtained in deuteriodichloromethane with a Perkin-Elmer EM-390 spectrometer. Electron paramagnetic resonance spectra were obtained on an Bruker ER 200B-SRC spectrometer at −110 °C. Absorption spectra were obtained with a Perkin-Elmer 330 spectrophotometer.

**Preparation of (Di-2-pyridylamine)(3,5-di-*tert*-butyl-*o*-semiquinonato)copper(II) Perchlorate–0.5-Tetrahydrofuran, [Cu(NH(py)$_2$)(DTBSQ)]ClO$_4$·0.5THF (1). Method A.** (Ethylene)(di-2-pyridylamine)copper(I) perchlorate, [Cu(NH(py)$_2$)(C$_2$H$_4$)]ClO$_4$, was dissolved in methanol. Dioxygen was bubbled through the flask at room temperature to yield a dark blue solution. Addition of diethyl ether yielded dark blue crystals of [Cu$_2$(NH(py)$_2$)$_2$(OCH$_3$)$_2$](ClO$_4$)$_2$. Anal. Calcd for C$_{22}$H$_{24}$Cl$_2$Cu$_2$N$_6$O$_{10}$: C, 36.18; H, 3.31; N, 11.50. Found: C, 36.20; H, 3.39; N, 11.32. To this Cu(II) dimer (0.50 g, 0.685 mmol) in approximately 15 mL of methanol was added 3,5-di-*tert*-butylcatechol, DTBC (0.152 g, 0.685 mmol). The resulting green solution was stirred for 0.5 h. A white precipitate formed and was removed by filtration. The solvent was removed from the filtrate under high vacuum to yield a green solid. Recrystallization from THF–petroleum ether yielded dark green crystals of **1**. Anal. Calcd for C$_{26}$H$_{33}$ClCuN$_3$O$_{6.5}$: C, 52.88; H, 5.63; N, 7.11. Found: C, 52.65; H, 5.55; N, 7.18. IR (cm$^{-1}$): 3340 m, 3270 w, 3230 w, 3165 w, 3130 w, 3100 w, 3040 w, 1650 s, 1620 w, 1595 s, 1580 m, 1535 s, 1340 w, 1305 w, 1245 w, 1240 m, 1210 w, 1165 m, 1125 s, 1095 s, 1060 s, 1030 w, 990 m, 965 w, 930 w, 915 m, 865 w, 860 m, 830 w, 810 w, 765 s, 750 w, 740 w, 725 w, 685 w, 670 w, 620 m.

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**Method B.** To $[Cu(NH(py)_2)(C_2H_4)]ClO_4$ (0.400 g, 1.10 mmol) in 20 mL of methanol was added 3,5-di-*tert*-butyl-1,2-benzoquinone, DTBQ (0.242 g, 1.10 mmol). The resulting dark green solution was stirred for 0.5 h and then filtered. Removal of solvent under high vacuum yielded a green powder. Recrystallization from THF–petroleum ether at room temperature yielded dark green crystals. Anal. Calcd for $C_{26}H_{33}ClCuN_3O_{6.5}$. Found: C, 52.54; H, 5.53; N, 7.03. IR data are identical with those listed above.

**Preparation of (*N,N,N',N'*-Tetramethylethylenediamine)(3,5-di-*tert*-butyl-*o*-semiquinonato)copper(II) Perchlorate, [Cu(TMEN)(DTBSQ)]ClO$_4$ (2).** This compound was prepared by method A. Adding dioxygen to $[Cu(TMEN)(C_2H_4)]ClO_4$ in methanol yielded $[Cu_2(TMEN)_2(OH)(OCH_3)](ClO_4)_2$. Anal. Calcd for $C_{13}H_{36}Cl_2Cu_2N_4O_{10}$: C, 25.74; H, 5.98; N, 9.24. Found: C, 25.66; H, 6.05; N, 9.20. Green crystals of **2** were obtained by recrystallization from THF–petroleum ether at room temperature. Anal. Calcd for $C_{20}H_{36}ClCuN_2O_6$: C, 48.09; H, 7.26; N, 5.61. Found: C, 47.86; H, 7.23; N, 5.80. IR ($cm^{-1}$): 1625 m, 1530 s, 1305 w, 1285 m, 1265 w, 1245 m, 1205 m, 1170 w, 1130 s, 1105 s, 1050 s, 1020 m, 995 w, 985 w, 955 m, 930 m, 905 w, 870 w, 860 s, 830 w, 810 s, 785 m, 765 m, 750 w, 720 w, 680 w, 650 w, 620 m.

**Preparation of (*N,N,N',N'*-Tetraethylethylenediamine)(3,5-di-*tert*-butyl-*o*-semiquinonato)copper(II) Perchlorate, [Cu(TEEN)(DTBSQ)]ClO$_4$ (3).** This compound was prepared by method B. Anal. Calcd for $C_{24}H_{44}ClCuN_2O_6$: C, 51.88; H, 7.98; N, 5.04. Found: C, 51.54; H, 7.44; N, 4.90. IR ($cm^{-1}$): 1580 s, 1540 s, 1340 w, 1335 w, 1305 m, 1255 m, 1245 s, 1210 w, 1185 w, 1180 w, 1175 w, 1130 s, 1050 s, 1020 w, 990 m, 930 m, 910 m, 875 w, 855 s, 830 m, 815 w, 805 m, 785 m, 765 m, 750 m, 725 s, 680 w, 655 w, 620 s.

**Preparation of (2,2'-Bipyridine)(3,5-di-*tert*-butyl-*o*-semiquinonato)copper(II) Perchlorate, [Cu(bpy)(DTBSQ)]ClO$_4$ (4).** This compound was prepared by method A. Adding dioxygen to $[Cu(bpy)(C_2H_4)]ClO_4$ yielded $[Cu_2(bpy)_2(OH)(OCH_3)](ClO_4)_2$·MeOH. Anal. Calcd for $C_{22}H_{24}Cl_2Cu_2N_4O_{11}$: C, 36.78; H, 3.37; N, 7.80. Found: C, 36.73; H, 3.25; N, 7.94. Green crystals of **4** were obtained by recrystallization from THF–petroleum ether at room temperature. Anal. Calcd for $C_{24}H_{28}ClCuN_2O_6$: C, 53.43; H, 5.23; N, 5.19. Found: C, 53.71; H, 4.96; N, 4.96. IR ($cm^{-1}$): 3130 w, 3090 w, 1615 m, 1605 m, 1580 m, 1570 w, 1560 w, 1530 m, 1515 m, 1500 m, 1320 m, 1305 w, 1290 w, 1265 w, 1255 m, 1245 m, 1230 w, 1205 w, 1175 w, 1160 m, 1125 s, 1110 s, 1055 s, 1045 s, 1035 s, 990 m, 930 w, 910 w, 865 m, 825 m, 805 w, 775 s, 750 w, 735 m, 685 w, 670 w, 655 w, 650 w, 620 m.

**Preparation of (1,10-Phenanthroline)(3,5-di-*tert*-butyl-*o*-semiquinonato)copper(II) Perchlorate–1-Tetrahydrofuran, [Cu(OP)(DTBSQ)]ClO$_4$·THF (5).** This compound was prepared by method A. Adding dioxygen to $[Cu(OP)(C_2H_4)]ClO_4$ yields $[Cu_2(OP)_2(OCH_3)_2](ClO_4)_2$. Anal. Calcd for $C_{26}H_{22}Cl_2Cu_2N_4O_{10}$: C, 41.72; H, 2.96; N, 7.49. Found: C, 41.57; H, 3.23; N, 7.09. Green crystals of **5** were obtained by recrystallization from THF–petroleum ether at room temperature. Anal. Calcd for $C_{30}H_{36}ClCuN_2O_7$: C, 56.69; H, 5.71; N, 4.41. Found: C, 56.56; H, 5.56; N, 4.39. IR ($cm^{-1}$): 3060 w, 1630 w, 1610 w, 1580 m, 1520 s, 1345 w, 1305 w, 1260 w, 1245 m, 1230 w, 1200 w, 1155 s, 1120 s, 1080 s, 1045 s, 985 m, 960 w, 925 w, 910 w, 875 m, 855 s, 825 w, 805 w, 785 w, 780 w, 740 w, 720 s, 650 w, 620 m.

**X-ray Data Collection and Structure Solution and Refinement for [Cu(NH(py)$_2$)(DTBSQ)]ClO$_4$·0.5THF (1).** Crystals suitable for diffraction were obtained by vapor diffusion at room temperature of petroleum ether into a THF solution of **1** prepared by method B. A black plate-shaped crystal of dimensions 0.29 × 0.06 × 0.40 mm was handled in the manner described elsewhere,[8] was then placed on a Syntex P3 diffractometer, and was shown to be suitable for diffraction on the basis of $\omega$ scans, which showed the peak width at half-height to be ca. 0.31° at −100 °C. The cell parameters were refined on the basis of 48 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 $\omega$-scan technique, intensity measurements of standard reflections, and data processing were performed as described elsewhere.[8] The solution and refinement of the structure were carried out on a Digital Equipment VAX 11/780 computer with a system of programs developed by J.C.C. The copper atoms were located by direct methods. The positions of the remaining nonhydrogen 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.[8] Atomic scattering factors and anomalous dispersion terms were taken from the usual sources.[9] Hydrogen atom positions were calculated with a C–H distance of 0.95 Å. The perchlorate group containing Cl(2) is disordered in a complicated pattern. The oxygen multiplicities were refined as follows: O(9), 0.7; O(9'), 0.3; O(10), 0.5; O(10'), 0.5; O(11), 0.6; O(11'), 0.4; O(12), 0.6; O(12'), 0.4. Atoms O(10), O(10'), and O(11') were not refined anisotropically. Least-squares refinement converged to $R = 0.050$ and $R_w = 0.044$, where $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$ with $w$ proportional to $1/[\sigma^2(I) + (0.03I)^2]$. The final difference map shows electron density near atom C(63) (0.59 e/Å$^3$) and near each copper atom (0.4 e/Å$^3$).

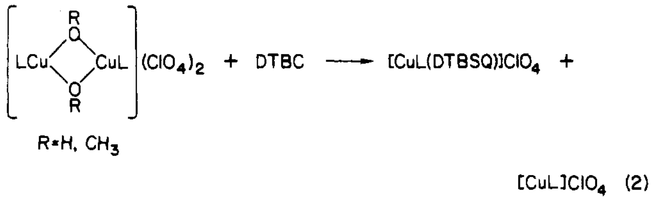
**Table I.** Crystal Data for [Cu(NH(py)$_2$)(DTBSQ)]ClO$_4$·0.5THF (**1**)

| | |
|---|---|
| mol formula | $C_{26}H_{33}ClCuN_3O_{6.5}$ |
| mol wt | 590.56 |
| $a$, Å | 14.794 (4) |
| $b$, Å | 19.513 (4) |
| $c$, Å | 9.766 (2) |
| $\alpha$, deg | 90.74 (2) |
| $\beta$, deg | 105.37 (2) |
| $\gamma$, deg | 93.79 (2) |
| $V$, Å$^3$ | 2708 |
| $Z$ | 4 |
| space group | $P\bar{1}$ |
| radiation | Mo K$\alpha$ ($\lambda$ = 0.71069 Å) from graphite monochromator |
| 2$\theta$ limit, deg | 4–43 |
| temp, °C | −100 |
| abs coeff, $cm^{-1}$ | 9.514 |
| no. of reflcns collected | 6704 |
| no. of unique reflcns | 6210 |
| unique data used ($I > 2\sigma(I)$) | 4107 |
| no. of variables | 697 |
| $R$ | 0.050 |
| $R_w$ | 0.044 |

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), and structure factor amplitudes (Table V) and a complete listing of bond distances and angles (Table VI) are available.[10]

## Results

**Synthesis and Properties.** The syntheses of Cu(II)–semiquinone complexes with bidentate nitrogen-donor ligands are straightforward and are presented in eq 2 and 3. These reactions involve



(2)

$$[CuL(C_2H_4)]ClO_4 + DTBBQ \rightarrow [CuL(DTBSQ)]ClO_4 + C_2H_4 \quad (3)$$

one-electron oxidation of the catechol (eq 2) or one-electron reduction of the corresponding benzoquinone (eq 3) to give the Cu(II)–semiquinone complex in excellent yields (>85%). Copper ions accept or donate the electrons in each case. An insoluble cuprous complex containing the ligand L and a perchlorate anion precipitates from methanol solutions during the preparation of DTBSQ complexes according to eq 2. In the presence of ethylene, the Cu(I)–ethylene complex $[CuL(C_2H_4)_2]ClO_4$ is obtained. When this reaction is run in the presence of 0.5 equiv of DTBBQ (in addition of DTBC), the only isolated product is the Cu(II)–DTBSQ complex. Use of excess DTBC does not increase the yield of the semiquinone product. The procedure outlined in eq 3 yields the same Cu(II)–DTBSQ complexes as those produced by the first method. Adding DTBBQ to the colorless Cu(I)–ethylene complexes immediately produces the green Cu(II) complexes. This procedure is the easier and cleaner of the two reactions.

These preparations yield green or blue-green crystalline solids that have similar physical and spectroscopic properties and reactivities. All of the compounds are stable under an inert atmosphere and give excellent elemental analyses for the indicated

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

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

**Table II.** Final Atomic Coordinates (×10 000) with Estimated Deviations for $[Cu(NH(py)_2)(DTBSQ)]ClO_4 \cdot 0.5THF$

| atom | *x* | *y* | *z* | atom | *x* | *y* | *z* |
|---|---|---|---|---|---|---|---|
| Cu(1) | 8294.3 (6) | 3474.3 (4) | 7561.1 (9) | C(14) | 7496 (5) | 232 (4) | 7807 (7) |
| Cu(2) | 3239.0 (6) | 3684.6 (5) | 7009.8 (9) | C(20) | 7786 (5) | 3021 (4) | 4630 (7) |
| Cl(1) | 792 (1) | 3607 (1) | 6527 (2) | C(21) | 7818 (5) | 2981 (4) | 3242 (8) |
| Cl(2) | 5778 (1) | 3459 (1) | 6850 (2) | C(22) | 8176 (5) | 3543 (4) | 2668 (7) |
| O(1) | 7968 (3) | 2480 (2) | 7359 (5) | C(23) | 8464 (5) | 4129 (4) | 3494 (7) |
| O(2) | 8822 (3) | 3252 (2) | 9558 (4) | C(24) | 8409 (5) | 4136 (4) | 4907 (7) |
| O(3) | 3201 (3) | 2705 (2) | 6641 (5) | C(25) | 8775 (5) | 4929 (4) | 7076 (7) |
| O(4) | 3688 (3) | 3427 (2) | 9006 (4) | C(26) | 9084 (5) | 5617 (4) | 7507 (8) |
| O(5) | 112 (3) | 3394 (3) | 7259 (6) | C(27) | 9140 (5) | 5825 (4) | 8863 (8) |
| O(6) | 681 (4) | 4314 (3) | 6182 (6) | C(28) | 8897 (5) | 5370 (4) | 9800 (8) |
| O(7) | 1706 (4) | 3558 (3) | 7464 (5) | C(29) | 8635 (5) | 4705 (4) | 9319 (7) |
| O(8) | 702 (5) | 3217 (3) | 5283 (6) | C(31) | 3610 (4) | 2385 (4) | 7756 (7) |
| O(9) | 5103 (6) | 3852 (5) | 7347 (10) | C(32) | 3812 (4) | 1681 (3) | 7735 (7) |
| O(9′) | 5243 (16) | 3997 (10) | 6285 (31) | C(33) | 4306 (4) | 1437 (3) | 8993 (7) |
| O(10) | 6721 (7) | 3641 (5) | 7817 (11) | C(34) | 4621 (4) | 1838 (4) | 10314 (7) |
| O(10′) | 6688 (7) | 3825 (6) | 7374 (11) | C(35) | 4382 (5) | 2493 (4) | 10335 (7) |
| O(11) | 5626 (9) | 3619 (7) | 5399 (10) | C(36) | 3897 (5) | 2798 (4) | 9059 (7) |
| O(11′) | 5598 (13) | 3002 (10) | 7778 (20) | C(37) | 5184 (5) | 1492 (4) | 11620 (7) |
| O(12) | 5551 (7) | 2751 (5) | 6957 (12) | C(38) | 6090 (5) | 1262 (4) | 11304 (8) |
| O(12′) | 5862 (12) | 3051 (10) | 5648 (16) | C(39) | 4616 (6) | 864 (4) | 11959 (8) |
| O(13) | 1483 (5) | 883 (4) | 9313 (8) | C(40) | 5461 (5) | 1985 (4) | 12916 (7) |
| N(1) | 8092 (4) | 3587 (3) | 5477 (6) | C(41) | 3488 (5) | 1237 (3) | 6385 (7) |
| N(2) | 8696 (4) | 4749 (3) | 5684 (6) | C(42) | 2402 (5) | 1212 (4) | 5858 (8) |
| N(3) | 8577 (4) | 4468 (3) | 7977 (6) | C(43) | 3914 (5) | 1543 (4) | 5237 (7) |
| N(4) | 3092 (4) | 3879 (3) | 4972 (6) | C(44) | 3772 (5) | 504 (4) | 6609 (8) |
| N(5) | 3803 (4) | 5011 (3) | 5465 (6) | C(50) | 2780 (5) | 3349 (4) | 4002 (8) |
| N(6) | 3383 (4) | 4667 (3) | 7532 (6) | C(51) | 2915 (6) | 3359 (4) | 2679 (8) |
| C(1) | 8260 (4) | 2165 (4) | 8535 (7) | C(52) | 3354 (6) | 3927 (5) | 2283 (8) |
| C(2) | 8126 (4) | 1441 (3) | 8664 (6) | C(53) | 3645 (5) | 4482 (4) | 3196 (8) |
| C(3) | 8531 (4) | 1193 (3) | 9964 (7) | C(54) | 3497 (5) | 4443 (4) | 4571 (8) |
| C(4) | 9065 (4) | 1603 (4) | 11184 (6) | C(55) | 3744 (5) | 5148 (4) | 6823 (8) |
| C(5) | 9162 (5) | 2297 (4) | 11063 (7) | C(56) | 4066 (5) | 5810 (4) | 7432 (10) |
| C(6) | 8762 (5) | 2593 (4) | 9756 (7) | C(57) | 3992 (6) | 5948 (4) | 8779 (10) |
| C(7) | 9497 (5) | 1233 (3) | 12539 (7) | C(58) | 3587 (6) | 5471 (4) | 9472 (8) |
| C(8) | 10244 (5) | 778 (4) | 12254 (7) | C(59) | 3291 (5) | 4844 (4) | 8833 (8) |
| C(9) | 8743 (5) | 774 (4) | 12974 (7) | C(61) | 664 (7) | 1075 (5) | 8327 (10) |
| C(10) | 9975 (5) | 1735 (4) | 13779 (8) | C(62) | 758 (6) | 1820 (4) | 8192 (10) |
| C(11) | 7556 (5) | 982 (4) | 7412 (7) | C(63) | 1361 (7) | 2088 (5) | 9595 (12) |
| C(12) | 6558 (5) | 1217 (4) | 6919 (7) | C(64) | 1981 (6) | 1483 (7) | 10031 (11) |
| C(13) | 8029 (5) | 1025 (4) | 6184 (7) | | | | |

formulations. The solvated compounds (**1** and **5**) do not lose solvent on standing at room temperature. Exposure of THF solutions to molecular oxygen yields DTBBQ and pale-blue precipitates. Addition of pyridine to THF solutions also generates DTBBQ; the copper-containing products from this reaction were not isolated.

**Description of the Structure of $[Cu(NH(py)_2)(DTBSQ)]ClO_4 \cdot 0.5THF$ (1).** The overall structure of **1** is apparent in the drawing of the molecule (Figure 1) and consists of two $[Cu(NH(py)_2)(DTBSQ)]^+$ cations bridged by a perchlorate anion. The second perchlorate anion and THF molecule are also associated with this dimer. Each copper ion is coordinated to two pyridyl nitrogen atoms from a $NH(py)_2$ ligand and two oxygen atoms from the DTBSQ ligand in an approximately planar arrangement. In addition, the perchlorate anions are coordinated in the axial positions to form distorted-octahedral geometries about each copper atom. When the interaction between Cu(1) and O(5) in an adjacent cell is considered, the crystal structure shows an infinite $Cu-ClO_4-Cu$ chain with long (2.795 (5) Å) and short (2.420 (5)–2.688 (8) Å) Cu–O interactions. This arrangement of cations and anions is similar to that of another perchlorate salt of a $Cu(II)-NH(py)_2$ complex.[11] The coordination spheres about the Cu(II) ions are not identical. The dihedral angle for the planes defined by the copper and nitrogen atoms and by the copper and oxygen atoms are 14.2° for Cu(1) and 7.1° for Cu(2). The THF molecule is not coordinated to either of the cations.

Selected bond distances and angles are presented in Table VII. The observed bond distances and angles for $NH(py)_2$ are nearly identical with those determined previously[1] and are not tabulated here.[10] Also, values for only one of the DTBSQ groups are listed; the second ring is identical within experimental error.[10] There are no unusual features in the copper coordination spheres. The Cu–N and all Cu–O distances are characteristic of distorted octahedrally coordinated Cu(II) complexes.[11,12] The C–O dis-

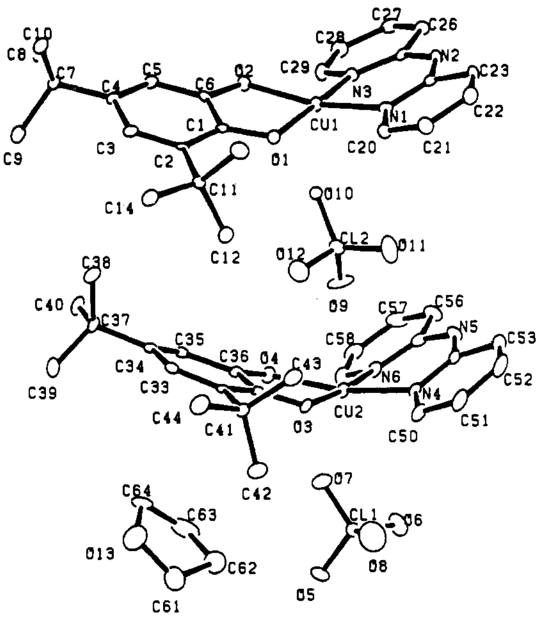

**Figure 1.** View of $[Cu(NH(py)_2)(DTBSQ)]ClO_4 \cdot 0.5THF$ (**1**). The vibrational ellipsoids are drawn at the 50% level. Hydrogen atoms are not shown.

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**Table VII.** Selected Bond Distances (Å) and Angles (deg) for $[Cu(NH(py)_2)(DTBSQ)]ClO_4 \cdot 0.5THF$

| | | | |
|---|---|---|---|
| Cu(1)–O(1) | 1.962 (5) | O(1)–C(1) | 1.293 (7) |
| Cu(1)–O(2) | 1.964 (4) | O(2)–C(6) | 1.304 (7) |
| Cu(2)–O(3) | 1.934 (5) | O(3)–C(31) | 1.289 (7) |
| Cu(2)–O(4) | 1.969 (4) | O(4)–C(36) | 1.284 (4) |
| Cu(1)–N(1) | 1.992 (6) | C(1)–C(2) | 1.427 (9) |
| Cu(1)–N(3) | 1.970 (6) | C(1)–C(6) | 1.446 (9) |
| Cu(2)–N(4) | 1.986 (6) | C(2)–C(3) | 1.362 (8) |
| Cu(2)–N(6) | 1.960 (6) | C(2)–C(11) | 1.527 (9) |
| Cu(1)–O(5) | 2.795 (5) | C(3)–C(4) | 1.442 (9) |
| Cu(1)–O(10) | 2.448 (10) | C(4)–C(5) | 1.361 (9) |
| Cu(2)–O(7) | 2.420 (5) | C(4)–C(7) | 1.523 (9) |
| Cu(2)–O(9) | 2.688 (8) | C(5)–C(6) | 1.407 (9) |
| O(13)–C(61) | 1.410 (11) | C(7)–C(8) | 1.539 (9) |
| O(13)–C(64) | 1.413 (12) | C(7)–C(9) | 1.535 (9) |
| C(61)–C(62) | 1.462 (12) | C(7)–C(10) | 1.533 (10) |
| C(62)–C(63) | 1.490 (12) | C(11)–C(12) | 1.531 (9) |
| C(63)–C(64) | 1.538 (14) | C(11)–C(13) | 1.538 (9) |
| | | C(11)–C(14) | 1.522 (10) |

| | | | |
|---|---|---|---|
| O(1)–Cu(1)–O(2) | 82.5 (2) | Cu(1)–O(1)–C(1) | 112.9 (4) |
| O(3)–Cu(2)–O(4) | 83.3 (2) | Cu(1)–O(2)–C(6) | 112.2 (4) |
| O(1)–Cu(1)–N(1) | 93.5 (2) | C(2)–C(1)–C(6) | 120.2 (6) |
| O(1)–Cu(1)–N(3) | 173.2 (2) | C(1)–C(2)–C(11) | 121.2 (6) |
| O(2)–Cu(1)–N(1) | 163.6 (2) | C(1)–C(2)–C(3) | 115.8 (6) |
| O(2)–Cu(1)–N(3) | 92.3 (2) | C(3)–C(2)–C(11) | 123.0 (6) |
| O(3)–Cu(2)–N(4) | 91.8 (2) | C(2)–C(3)–C(4) | 125.2 (6) |
| O(3)–Cu(2)–N(6) | 174.6 (2) | C(3)–C(4)–C(5) | 118.5 (6) |
| O(4)–Cu(2)–N(4) | 166.0 (2) | C(3)–C(4)–C(7) | 117.9 (6) |
| O(4)–Cu(2)–N(6) | 92.3 (2) | C(5)–C(4)–C(7) | 123.6 (6) |
| N(1)–Cu(1)–N(3) | 92.7 (2) | C(4)–C(5)–C(6) | 119.7 (6) |
| N(4)–Cu(2)–N(6) | 91.8 (3) | C(1)–C(6)–C(5) | 120.5 (6) |
| C(61)–O(13)–C(64) | 108.5 (8) | C(4)–C(7)–C(9) | 110.4 (6) |
| C(61)–C(62)–C(63) | 105.1 (8) | C(4)–C(7)–C(10) | 112.2 (6) |
| C(62)–C(63)–C(64) | 100.3 (8) | C(4)–C(7)–C(8) | 108.6 (5) |
| C(9)–C(7)–C(10) | 108.7 (6) | C(8)–C(7)–C(10) | 108.2 (6) |
| C(2)–C(11)–C(13) | 109.6 (5) | C(8)–C(7)–C(9) | 108.7 (6) |
| C(2)–C(11)–C(12) | 109.6 (5) | C(12)–C(11)–C(14) | 108.5 (6) |
| C(2)–C(11)–C(14) | 111.8 (5) | C(12)–C(11)–C(13) | 109.9 (6) |
| C(13)–C(11)–C(14) | 107.4 (6) | | |

**Table VIII.** Visible Absorption Data for Cu(II)–3,5-Di-*tert*-butyl-*o*-semiquinone Complexes, $[CuL(DTBSQ)]ClO_4$

| L | λ, nm | ε, $M^{-1}$ $cm^{-1}$ | L | λ, nm | ε, $M^{-1}$ $cm^{-1}$ |
|---|---|---|---|---|---|
| $NH(py)_2$ (**1**) | 810 | 300 | bpy (**4**) | 811 | 380 |
| | 387 | 2500 | | 391 | 2900 |
| TMEN (**2**) | 815 | 340 | OP (**5**) | 822 | 290 |
| | 387 | 2500 | | 391 | 2500 |
| TEEN (**3**) | 770 | 680 | | | |
| | 384 | 3000 | | | |

tances of the DTBSQ ligands (1.284 (8)–1.304 (7) Å) are characteristic of DTBSQ complexes, for which distances of 1.28 Å are typical.[6] The C–O bond lengths of coordinated catechol are longer than this value (1.35 Å), whereas these bond lengths for the corresponding quinone are shorter (1.234 (4) Å).[6] The Cu–N, Cu–O, and C–O bond lengths are thus all consistent with the formulation of **1** as a Cu(II)–semiquinone complex.

**Spectroscopy.** The spectral properties of compounds **1**–**5** are consistent with the indicated formulations. All are EPR silent at liquid-nitrogen temperatures, a result expected for the complex formed by the coordination of a Cu(II) ion with one unpaired electron to a semiquinone ligand also with one unpaired electron. Similar results were obtained for a Cu(II)–semiquinone complex prepared electrochemically.[7] All of the compounds reported here have similar visible absorption spectra. Data are summarized in Table VIII; the spectrum of **1** is shown in Figure 2. All complexes have an absorption maximum in the 700–900-nm region of moderate intensity and a sharp, intense band in the 380–395-nm region. These features are similar to those of free 3,5-di-*tert*-butyl-*o*-semiquinone (although of less intensity)[7,13] and differ significantly from those of Cu(II)–catecholate complexes.[7,13,14] The spectral features of **1**–**5** are similar to those of $Cu(DTBC)(DTBSQ)^-$ prepared electrochemically.[7]

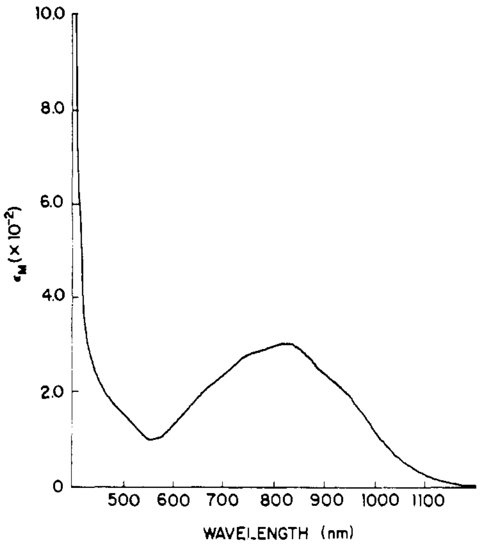

**Figure 2.** Visible absorption spectrum of $[Cu(NH(py)_2)(DTBSQ)]ClO_4 \cdot 0.5THF$ (**1**).

## Discussion

In this study, we establish the basic features of Cu(II)–*o*-semiquinone coordination chemistry. These complexes are prepared by the one-electron oxidation of the catechol by basic Cu(II) dimers (eq 2) or by the one-electron reduction of the corresponding *o*-benzoquinone by Cu(I)–ethylene complexes (eq 3). All of the complexes **1**–**5** have similar spectroscopic properties (Table VIII) and are indefinitely stable under an inert atmosphere. Solids yield excellent elemental analyses for the indicated formulations.

Our results demonstrate that catechol oxidation by basic Cu(II) complexes proceeds in one-electron-transfer steps. The hydroxy- and methoxy-bridged Cu(II) dimers are formed from the reaction of dioxygen with Cu(I)–ethylene complexes and are similar to those proposed as active catalysts in other systems that carry out the copper-catalyzed oxidation of catechols to *o*-benzoquinones.[3,4] The nature of the Cu(II)–catechol complexes formed during these reactions has not been established, although several structures have been proposed.[3-5] Importantly, the single-step two-electron oxidation of catechol by such basic Cu(II) complexes is not observed; rather, *o*-benzoquinone is obtained only after exposure of **1**–**5** to dioxygen or by the addition of small molecules such as pyridine.

The structural characterization of **1** establishes this complex as a Cu(II)–*o*-semiquinone complex. The similarity in properties between **1** and **2**–**5** suggests that these other compounds have similar structures. The carbon–oxygen bond lengths of the coordinated DTBSQ ligand (1.284 (8)–1.304 (7) Å) in **1** are characteristic of this ligand (1.283 (5)–1.285 (7) Å) in general. The Cu–N and Cu–O distances as well as the overall geometry of the complex are typical of Cu(II) complexes. The structural study also confirms the presence of one THF molecule per two $[Cu(NH(py)_2)(DTBSQ)]$ cations; there is no interaction between

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*Inorg. Chem.* **1985**, *24*, 3171–3176 **3171**

the solvent molecule and these cations. Formation of solvates is common for catechol derivatives.[6] Loss of solvent has frequently made characterization of these complexes by analytical methods difficult. The THF solvates reported here (**1** and **5**) appear to be stable to loss of solvent.

## Conclusions

This work establishes that Cu(II)–DTBSQ complexes can be prepared and characterized analytically, spectroscopically, and structurally. Preparative methods and spectroscopic and structural features are similar to those of other metal–DTBSQ complexes.[6,7,13] Our complexes are stable to further reduction to Cu(I) ions and the *o*-benzoquinone in the absence of small molecules such as pyridine. However, exposure to dioxygen yields a Cu(II) species and *o*-benzoquinone. These results suggest that the formation of *o*-semiquinone species should be considered in the copper-catalyzed oxidation of catechols by copper complexes and dioxygen.[15]

**Acknowledgment.** The technical assistance of R. M. Swiatek and L. Lardear is gratefully acknowledged.

**Registry No.** **1**, 97467-47-5; **2**, 97467-49-7; **3**, 97467-51-1; **4**, 97467-53-3; **5**, 97467-55-5; $[Cu(NH(py)_2)(C_2H_4)]ClO_4$, 91128-06-2; $[Cu_2(NH(py)_2)(OCH_3)_2](ClO_4)_2$, 97486-05-0; $[Cu(TMEN)(C_2H_4)]ClO_4$, 93757-51-8; $[Cu(TMEN)_2(OH)(OCH_3)](ClO_4)_2$, 97467-57-7; $[Cu(TEEN)(C_2H_4)]ClO_4$, 93757-58-5; $[Cu(bpy)(C_2H_4)]ClO_4$, 93757-62-1; $[Cu_2(bpy)_2(OH)(OCH_3)](ClO_4)_2$, 97467-59-9; $[Cu(OP)(C_2H_4)]ClO_4$, 93757-69-8; $[Cu_2(OP)_2(OCH_3)_2](ClO_4)_2$, 97467-61-3.

**Supplementary Material Available:** General temperature factors (Table III), calculated hydrogen atom positions (Table IV), structure factor amplitudes (Table V), and complete bond distances and angles (Table VI) (16 pages). Ordering information is given on any current masthead page.

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(15) (a) All of the compounds reported here, including the Cu(I)–ethylene complexes and the Cu(II)–DTBSQ complexes, are catalytically active in the oxidation of DTBC in DTBBQ, as determined by literature procedures.[5a,15b] (b) Oishi, N.; Nishida, Y.; Ida, K.; Kida, S. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 2847–2850.

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# Preparation and X-ray and Neutron Diffraction Structure Determination of the Chlorotrihydroborate Ion, $[BH_3Cl]^-$

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In the course of attempts to grow a single crystal of the $[PPN]^+$ salt of the heptahydrodiborate anion, $[(Ph_3P)_2N]^+[B_2H_7]^-$, for X-ray and neutron diffraction analysis, prolonged exposure of $[B_2H_7]^-$ to the mother liquor $[CH_2Cl_2/(C_2H_5)_2O]$ yielded colorless crystals containing a new anion, $[(Ph_3P)_2N]^+[BH_3Cl]^-\cdot CH_2Cl_2$. An improved synthetic procedure for $[BH_3Cl]^-$ was subsequently developed, and spectroscopic and structural analyses of $[(Ph_3P)_2N]^+[BH_3Cl]^-\cdot CH_2Cl_2$ were completed. The compound crystallizes in space group $P\bar{1}$ with the following cell parameters at 90 K: $a = 9.514$ (1) Å, $b = 10.495$ (3) Å, $c = 16.982$ (9) Å, $\alpha = 90.74$ (4)°, $\beta = 93.89$ (5)°, $\gamma = 94.44$ (2)°, $V = 1686$ (2) Å$^3$, $Z = 2$. The structure was refined to yield the following agreement factors: for the X-ray analysis (carried out at 105 K), $R_F = 0.075$ and $R_{wF} = 0.095$ for 5588 reflections with $I > 3\sigma(I)$; for the neutron analysis (carried out at 90 K), $R_F = 0.071$ and $R_{wF} = 0.069$ for 2917 reflections with $I > 3\sigma(I)$. The $[BH_3Cl]^-$ anion has an approximately tetrahedral geometry in which the B–Cl bond, however, is unusually long [2.003 (8) Å], due to the fact that $[PPN]^+[BH_3Cl]^-$ is cocrystallized with a small amount (12–19%) of its precursor, $[PPN]^+[B_2H_7]^-$.

## Introduction

A number of adducts formed by anions with $BH_3$ are known, the most familiar being $[BH_4]^-$ ($BH_3 + H^-$). Among other such adducts, the best known is the cyanotrihydroborate(1–) anion, $[H_3BCN]^-$,[1-4] the first reported example of an adduct between $BH_3$ and a pseudohalide;[5] other known pseudohalide adducts of $BH_3$ are $[H_3BNC]^-$,[4] $[H_3BSCN]^-$,[3,6] $[H_3BNCS]^-$,[3] and $[H_3BN_3]^-$.[7] Attempts to prepare isolable salts of the corresponding halide adducts have been less successful. The only such adduct isolated prior to this study was $[H_3BF]^-$,[6] although $[H_3BCl]^-$ and $[H_3BBr]^-$ were reported by other investigators to be present in solution in the presence of other hydroborate anions.[8,9]

During attempts to grow crystals of $[PPN]^+[B_2H_7]^-$ [$PPN^+ = (Ph_3P)_2N^+$] from dichloromethane solutions,[10] one solution that had been allowed to stand for an extended period of time yielded crystals found to be isostructural with the $[B_2H_7]^-$ salt but to have the composition $[PPN]^+[H_3BCl]^-\cdot CH_2Cl_2$. This outcome was apparently the result of prolonged contact between the $[B_2H_7]^-$ anion and the solvent, resulting in the replacement of some of the $[BH_4]^-$ of $[B_2H_7]^-$ with $[Cl]^-$. We subsequently learned that other workers had reported a similar observation but had not isolated the products from reaction mixtures.[11] This encouraged us to develop a practical synthesis for the chlorotrihydroborate(1–) anion and to study the properties of some of its salts, as well as to investigate the possibility of preparing and isolating the corresponding bromide and iodide derivatives.

## Results and Discussion

**Preparation of $[PPN]^+[H_3BCl]^-$, $[Bu_4N]^+[H_3BCl]^-$, and $[Et_4N]^+[H_3BCl]^-$.** Tensimetric titrations of $[PPN]^+Cl^-$,

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