Counterligand Dependence of Charge Distribution in Copper–Quinone Complexes. Structural and Magnetic Properties of (3,5-Di-*tert*-butylcatecholato)(bipyridine)copper(II)
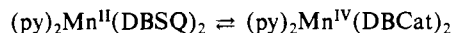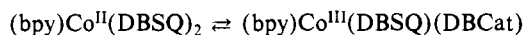
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Crystals of Cu(bpy)(DBCat) prepared under hydrous and anhydrous conditions have been studied crystallographically. Samples of the complex prepared in absolute ethanol crystallize in the orthorhombic crystal system, space group *Pbca*, with cell constants of $a = 15.731$ (4), $b = 14.204$ (4), and $c = 19.449$ (3) Å. Complex molecules are dimeric in structure, with Cu^{2+} ions in a square-pyramidal coordination geometry and four dimeric molecules per unit cell. Copper centers are bridged by oxygen atoms of adjacent catecholate ligands. Complex molecules in samples prepared in 50% ethanol and recrystallized from dichloromethane are monomeric and square planar in structure. Crystals obtained by this procedure form with both water and CH_2Cl_2 molecules of crystallization, Cu(bpy)(DBCat)·1.5CH₂Cl₂·0.5H₂O. Crystals form in the monoclinic crystal system, space group *I2/a*, in a cell of dimensions $a = 29.019$ (4) Å, $b = 9.982$ (2) Å, $c = 18.620$ (3) Å, and $\beta = 92.70$ (1)°, with $Z = 8$. The crystal structure consists of stacks of complex molecules with water molcules hydrogen bonded to catecholate oxygen atoms of adjacent stacks. EPR spectra recorded on solid samples of both forms of the complex show $\Delta M_s = 2$ transitions, indicating coupling between paramagnetic metal ions. Solution spectra recorded at room temperature in CH_2Cl_2 and also at 77 K indicate that the complex is monomeric under these conditions. However, spectra recorded at 77 K in a CH_2Cl_2/toluene glass indicate a dimeric structure with Cu–Cu coupling. EPR spectra recorded on complexes containing diphos and phosphorus–nitrogen donor ligands in place of bpy indicate that the quinone is the paramagnetic center. These results lead to the conclusion that, with soft donor ligands, the charge distribution for copper–quinone complexes is $Cu^I(SQ)$ but, with hard donor counterligands, it is $Cu^{II}(Cat)$.

Introduction

Studies carried out on transition-metal complexes containing semiquinone and catecholate ligands have shown that metal and quinone frontier electronic levels are often close in energy. Unlike related dithiolene and diimine complexes that have delocalized chelate rings,[2] a formal description of charge distribution appears to remain appropriate. Complexes containing *o*-benzoquinone, *o*-semiquinone, and catecholate ligands have been studied, and crystallographic structure determinations have proven to be an important means of assigning charge on both ligand and metal.[3] Carbon–oxygen bond lengths are indicative of quinone ligand charge and metal–oxygen lengths are often characteristic of metal ion charge and spin state. Conclusions drawn from these structural criteria are often substantiated by magnetic resonance, infrared, and Mössbauer data and by magnetic properties. Complexes of Co and Mn with nitrogen donor counterligands serve as good illustrations of the similarity between metal and quinone orbital energies, and the ability to differentiate between electronically different forms of the complex.[4,5] Co^{+2}/Co^{+3} and Mn^{+2}/Mn^{+4} forms of the 3,5-di-*tert*-butyl-1,2-semiquinone (DBSQ) and catecholate (DBCat) complexes

$$(bpy)Co^{II}(DBSQ)_2 \rightleftharpoons (bpy)Co^{III}(DBSQ)(DBCat)$$

$$(py)_2Mn^{II}(DBSQ)_2 \rightleftharpoons (py)_2Mn^{IV}(DBCat)_2$$

exist in thermal equilibrium in solution, related by transfer of one or two electrons to coordinated quinone ligands. Specific effects that stabilize one charge distribution over the other in these complexes remain poorly understood, but studies have shown that changes in properties which influence quinone and metal orbital energies can result in changes in charge distribution. For example, weak donor counterligands favor reduced-metal–oxidized-quinone complexes. Strong donor ligands contribute to higher d-orbital energies and result in complexes with oxidized metal ions bonded to reduced catecholate ligands. This effect is subtly apparent in

the tetrameric Co and Mn quinone complexes, $[M(DBSQ)_2]_4$, where weak bridging oxygen

$$[Mn^{II}(DBSQ)_2]_4 + py \rightleftharpoons Mn^{IV}(py)_2(DBCat)_2$$
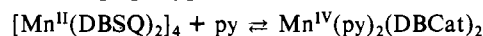
donors result in reduced divalent metal ions, relative to the monomeric nitrogen-donor adducts shown above.[6] In this report we describe work on a particularly clear-cut example of the counterligand influence upon charge distribution in the metal–quinone chelate ring.

Copper–catecholate complexes have been of interest for some time due primarily to the role of copper as a biological[7] or synthetic[8] catalyst for catechol and phenol oxidation. Brown has reported that Cu(bpy)(DBCat) reacts with O_2 to give the lactone

$$Cu(bpy)(DBCat) + O_2 \rightleftharpoons \quad + \quad \text{copper complexes} \quad (1)$$
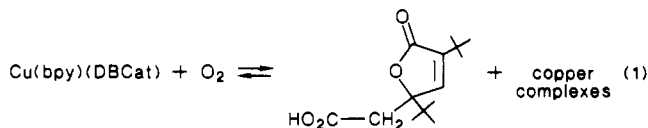
shown in eq 1.[9] Copper is also a metal ion which shows marked charge dependence upon the donor character of coordinated ligands. Hard donor nitrogen and oxygen ligands stabilize Cu(II), while complexes of phosphorus and sulfur ligands are most stable in the Cu(I) form. In this report we describe the counterligand dependence of the charge distribution within the copper–quinone chelate ring and provide structural characterization on forms of the 3,5-di-*tert*-butylcatecholate complex reported by Brown.[10,11]

Experimental Section

Reagent grade chemicals were used in all experiments, and solvents were purified by using standard procedures.

Cu(bpy)(DBCat)·0.5H₂O·1.5CH₂Cl₂. Copper complexes were prepared by a slight variation on the method described by Brown.[10]

(1) (a) University of Louisville. (b) University of Colorado. (c) On leave from Rhode Island College, Providence, RI.
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Table I. Crystal Data and Details of the Structure Determination for Cu(bpy)(DBCat)·1.5CH$_2$Cl$_2$·0.5H$_2$O

Crystal Data

formula	CuCl$_3$O$_{2.5}$N$_2$C$_{25.5}$H$_{32}$
color	purple
M_r	575.9
space group[a]	$I2/a$
cryst system	monoclinic
a,[b] Å	29.019 (4)
b, Å	9.982 (2)
c, Å	18.620 (3)
β, deg	92.70 (1)
V, Å^3	5387.4
d_{obsd}, g cm^{-3}	1.41 (1)
Z	8
d_{calcd}, g cm^{-3}	1.420
$F(000)$	2392
μ, cm^{-1}	11.6
cryst dimens, mm	0.41 × 0.36 × 0.33

Data Collection and Reduction[c]

diffractometer	Syntex P$\bar{1}$
data collcd	$+h,+k,\pm l$
radiation (λ, Å)	Mo Kα (0.710 69)
monochromator angle, deg	12.2
temp, K	294–296
scan technique	θ–2θ
scan range (2θ) min–max, deg	3.0–50.0
scan speed, deg/min	4.0
scan range	0.7° below Kα_1 and 0.7° above Kα_2
bkgd	stationary cryst–stationary counter; bkgd time = 0.5(scan time)
no. of unique reflcns measd	4050
no. of obsd reflcns	2182
criterion	$F > 6\sigma(F)$

Structure Determination and Refinement

scattering factors	neutral atoms[d]
R_1; R_2[e]	0.057; 0.061
wt	$1/(\sigma(F)^2 + 0.0005F^2)$
no. of params	308
ratio of observns to params	7.1
GOF	1.53

[a] *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1965; Vol. 1. [b] Cell dimensions were determined by least-squares fit of the setting angles of 30 reflections with 2θ in the range 15–22°. [c] The data reduction program was written in this laboratory. Other programs were contained in or derived from the Northwestern Crystallographic Computing Library of Dr. J. A. Ibers. [d] *International Tables for X-ray Crystallograph*; Kynoch: Birmingham, England, 1974; Vol. 4., pp 55–60, 99–101, 149–150. [e] The quantity minimized in the least-squares procedures is $\sum w(|F_o| - |F_c|)^2$. $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$. $R_2 = [\sum w(|F_o| - |F_c|)^2/\sum w(F_o)^2]^{1/2}$.

A solution of hydrated copper sulfate (0.80 g, 5 mmol) in 15 mL of water was added with stirring to a solution containing 1.11 g (5 mmol) of 3,5-di-*tert*-butylcatechol, 0.78 g (5 mmol) 2,2'-bipyridine, and 0.60 g (11 mmol) KOH in 25 mL of 50% aqueous ethanol. The resulting purple solid was filtered and recrystallized from dry dichloromethane under N$_2$. Crystals were isolated and stored at low temperature to retard loss of the dichloromethane solvate. The complex is soluble in chlorinated hydrocarbon solvents and slightly soluble in toluene.

Anal. Calcd for CuCl$_3$O$_{2.5}$N$_2$C$_{25.5}$H$_{32}$: C, 47.9; H, 5.0; Cl, 16.6. Found: C, 48.5; H, 5.2; Cl, 16.3.

[Cu(bpy)(DBCat)]$_2$. This form of the complex was prepared by using absolute ethanol as the solvent medium for the synthetic procedure above and by using anhydrous copper sulfate as the source of copper ion. Dark purple crystals suitable for crystallographic investigation were obtained by recrystallization from dichloromethane.

Anal. Calcd for CuO$_2$N$_2$C$_{24}$H$_{28}$: C, 65.5; H, 6.4. Found: C, 65.9; H, 6.5.

Cu(diphos)(DBSQ). This complex was prepared by procedures described by Razuvaev, with 1,2-bis(diphenylphosphino)ethane (diphos) used in place of triphenylphosphine.[12] Similar complexes containing phosphorus–nitrogen donor ligands were prepared by this same procedure

Table II. Atomic Positional Parameters for Cu(bpy)(DBCat)·0.5H$_2$O·1.5CH$_2$Cl$_2$

atom	x	y	z	U_{eq},[a] Å^2
Cu	0.21909 (3)	0.01964 (10)	0.29164 (5)	0.0393 (5)
O1	0.2027 (2)	0.1204 (5)	0.3732 (3)	0.044 (1)
O2	0.1595 (2)	-0.0519 (5)	0.2866 (3)	0.047 (1)
C1	0.1562 (2)	0.1079 (8)	0.3780 (4)	0.034 (1)
C2	0.1334 (2)	0.0141 (8)	0.3322 (4)	0.036 (1)
C3	0.0848 (2)	0.0004 (8)	0.3338 (4)	0.035 (1)
C4	0.0621 (2)	0.0849 (9)	0.3803 (4)	0.039 (1)
C5	0.0834 (3)	0.1785 (8)	0.4250 (4)	0.038 (1)
C6	0.1310 (3)	0.1867 (8)	0.4251 (4)	0.036 (1)
C7	0.0597 (3)	-0.0996 (8)	0.2829 (4)	0.042 (1)
C8	0.0658 (4)	-0.0610 (14)	0.2047 (6)	0.073 (3)
C9	0.0077 (4)	-0.1043 (12)	0.2927 (6)	0.071 (3)
C10	0.0793 (4)	-0.2425 (12)	0.2953 (7)	0.074 (3)
C11	0.0556 (3)	0.2752 (9)	0.4701 (4)	0.045 (2)
C12	0.0063 (4)	0.2228 (14)	0.4797 (8)	0.096 (4)
C13	0.0516 (5)	0.4090 (13)	0.4272 (8)	0.100 (4)
C14	0.0791 (5)	0.2925 (17)	0.5441 (7)	0.109 (4)
N1	0.2814 (2)	0.0998 (6)	0.2815 (3)	0.042 (1)
C15	0.2996 (3)	0.2032 (9)	0.3161 (5)	0.048 (1)
C16	0.3419 (3)	0.2570 (9)	0.3054 (5)	0.051 (1)
C17	0.3669 (3)	0.1966 (10)	0.2523 (5)	0.051 (1)
C18	0.3494 (3)	0.0895 (10)	0.2147 (5)	0.048 (1)
C19	0.3058 (2)	0.0412 (8)	0.2292 (4)	0.036 (1)
N2	0.2394 (2)	-0.0910 (6)	0.2094 (3)	0.041 (1)
C20	0.2143 (3)	-0.1876 (9)	0.1769 (4)	0.040 (1)
C21	0.2310 (3)	-0.2680 (9)	0.1241 (5)	0.048 (1)
C22	0.2754 (3)	-0.2441 (10)	0.1038 (5)	0.055 (1)
C23	0.3015 (3)	-0.1453 (10)	0.1363 (5)	0.049 (1)
C24	0.2827 (3)	-0.0637 (8)	0.1904 (4)	0.038 (1)
Cl1	0.20658 (8)	0.05059 (24)	0.03630 (13)	0.0711 (7)
Cl2	0.12157 (10)	-0.21596 (28)	0.01295 (16)	0.0864 (7)
Cl3	0.11095 (11)	-0.43163 (33)	0.11301 (16)	0.1116 (8)
C25	0.25	0.1471 (13)	0.0	0.052 (2)
C26	0.1148 (5)	-0.3872 (11)	0.0237 (6)	0.082 (2)
O3	0.25	0.4973 (11)	0.0	0.142 (4)

[a] $U_{eq} = {}^1/{}_3\sum U_{ii}$.

using 2-[2-(diphenylphosphino)ethyl]pyridine and the iminophosphine ligand of Rauchfuss, *o*-C$_6$H$_4$(PPh$_2$)(CHN-*p*-C$_6$H$_4$OCH$_3$).[13]

X-ray Structure Determination on Cu(bpy)(DBCat)·0.5H$_2$O·1.5CH$_2$Cl$_2$. A crystal suitable for crystallographic analysis was mounted on a glass fiber and coated with an amorphous resin to retard loss of dichloromethane solvate. The crystal was aligned on a Syntex P$\bar{1}$ automated diffractometer, and crystal quality was examined by using rotational and axial photographs. Information regarding the structure determination is given in Table I. Four standard reflections monitored during data collection showed only statistical fluctuations in intensity. Experiments carried out to estimate the effect of absorption indicated that correction was not necessary. The location of the Cu atom was determined from a sharpened Patterson map, and the locations of other atoms of the complex molecule were determined from phases generated from the Cu atom position. Solvate atom positions were determined from difference Fourier maps with phases generated by refinement of the complex molecule. Hydrogen atom positions were calculated, and the location of the water solvate hydrogen was determined from a difference Fourier map. Fixed contributions for all hydrogen atoms were included in final cycles of refinement. All non-hydrogen atoms of the structure were refined with anisotropic thermal parameters. The largest parameter shift on the final cycle of refinement occurred for U_{22} of C14 with a change of 0.10 relative to its esd. Greatest residual electron density was in the vicinity of C13 with a value of 0.36 e/Å^3. Final atomic coordinates are given in Table II. Tables containing anisotropic thermal parameters and structure factors are available as supplementary material.

X-ray Structure Determination on [Cu(bpy)(DBCat)]$_2$. A crystal of the complex was mounted and aligned on the diffractometer as before. Crystallographic information on this structure determination is contained in Table III. The structure was solved by the heavy-atom method. All non-hydrogen atoms of the structure were refined anisotropically. Fixed contributions for all hydrogen atoms were included in the final refinement. The largest parameter shift on the final cycle of refinement occurred for U_{11} of C13, with a change of 0.91 of its esd. Greatest residual electron density was found in the region of the *tert*-butyl group, including atoms C12, C13, and C14. This corresponded to 0.56 e/Å^3. Atomic

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Table III. Crystal Data and Details of the Structure Determination for [Cu(bpy)(DBCat)]$_2$

Crystal Data	
formula	$CuO_2N_2C_{24}H_{28}$
color	purple
M_r	439.7
space group^a	$Pbca$
cryst system	orthorhombic
$a,^b$ Å	15.731 (4)
b, Å	14.204 (3)
c, Å	19.449 (3)
V, Å^3	4345.8
d_{obsd}, g cm^{-3}	1.34 (1)
Z	8
d_{calcd}, g cm^{-3}	1.343
$F(000)$	1848
μ, cm^{-1}	10.6
cryst dimens, mm	0.45 × 0.40 × 0.38

Data Collection and Reduction^c	
diffractometer	Syntex P$\bar{1}$
data colled	$+h,+k,+l$
radiation (λ, Å)	Mo Kα (0.710 69)
monochromator angle, deg	12.2
temp, K	294–296
scan technique	θ–2θ
scan range (2θ) min–max, deg	3.0–50.0
scan speed, deg/min	4.0
scan range	0.7° below Kα_1 and 0.7° above Kα_2
bkgd	stationary cryst–stationary counter; bkgd time = 0.5(scan time)
no. of unique reflcns measd	4504
no. of obsd reflcns	2612
criterion	$F < 6\sigma(F)$

Structure Determination and Refinement	
scattering factors	neutral atoms^d
R_1; R_2	0.043; 0.055
wt	$1/(\sigma(F)^2 + 0.0005F^2)$
no. of params	262
ratio of observns to params	10.0
GOF	1.91

^{a}*International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1965; Vol. 1. ^{b}Cell dimensions were determined by least-squares fit of the setting angles of 25 reflections with 2θ in the range 15–22°. ^{c}The data reduction program was written in this laboratory. Other programs were contained in or derived from the Northwestern Crystallographic Computing Library of Dr. J. A. Ibers. ^{d}*International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. 4., pp 55–60, 99–101, 149–150. ^{e}The quantity minimized in the least-squares procedures is $\sum w(|F_o| - |F_c|)^2$. $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$. $R_2 = [\sum w(|F_o| - |F_c|)^2/\sum w(F_o)^2]^{1/2}$.

positions are given in Table IV. Tables containing anisotropic thermal parameters and structure factors are available as supplementary material.

Magnetic Measurements. Room-temperature magnetic susceptibility measurements were carried out on a PARC Model 155 vibrating-sample magnetometer at the University of Louisville. The balance was calibrated with Hg[Co(SCN)$_4$]. All X-band EPR spectra were recorded on a Varian E-109 spectrometer at the University of Louisville. Variable-temperature measurements were conducted by using an Oxford Instruments Cryogenic temperature control apparatus. Solution EPR spectra were recorded in dichloromethane and toluene solutions. Spectra were referenced to DPPH.

Results

Structural Features of Cu(O$_2$C$_6$H$_2$(t-Bu)$_2$)(N$_2$C$_{10}$H$_8$)·0.5H$_2$O·1.5CH$_2$Cl$_2$. Samples of Cu(bpy)(DBCat) prepared in a hydrated medium and recrystallized from dichloromethane form large monoclinic crystals that contain both water and dichloromethane molecules of crystallization. The complex molecule is four-coordinate and square planar, as shown in Figure 1. Bond distances and angles are given in Table V. The metal atom is displaced 0.028 Å from the O$_2$N$_2$ plane. Both ligands are planar and deviate only slightly from the plane of the inner coordination sphere. Copper–oxygen bond lengths are 1.870 (5) and 1.901 (5) Å for O2 and O1. The longest metal–oxygen length is to O1, which is hydrogen bonded to the water solvate molecule (Figure

Table IV. Atomic Positional Parameters for [Cu(bpy)(DBCat)]$_2$

atom	x	y	z	$U_{eq},^a$ Å^2
Cu	-0.00198 (2)	0.39775 (3)	0.02582 (2)	0.0358 (3)
O1	-0.0894 (1)	0.4744 (2)	-0.0127 (1)	0.041 (1)
O2	-0.0545 (1)	0.4176 (2)	0.1131 (1)	0.044 (1)
C1	-0.1490 (2)	0.4900 (2)	0.0361 (2)	0.034 (1)
C2	-0.1304 (2)	0.4600 (2)	0.1035 (2)	0.037 (1)
C3	-0.1907 (2)	0.4758 (2)	0.1557 (2)	0.042 (1)
C4	-0.2662 (2)	0.5206 (3)	0.1380 (2)	0.044 (1)
C5	-0.2855 (2)	0.5517 (2)	0.0719 (2)	0.041 (1)
C6	-0.2243 (2)	0.5358 (2)	0.0211 (2)	0.038 (1)
C7	-0.1734 (3)	0.4423 (3)	0.2294 (2)	0.053 (2)
C8	-0.2459 (3)	0.4649 (4)	0.2788 (2)	0.077 (2)
C9	-0.0932 (3)	0.4888 (4)	0.2595 (2)	0.074 (2)
C10	-0.1623 (3)	0.3370 (3)	0.2308 (2)	0.071 (2)
C11	-0.3665 (2)	0.6049 (3)	0.0559 (2)	0.053 (1)
C12	-0.3485 (4)	0.7084 (4)	0.0581 (5)	0.150 (4)
C13	-0.4382 (4)	0.5831 (6)	0.1058 (4)	0.148 (3)
C14	-0.3958 (4)	0.5837 (7)	-0.0193 (4)	0.166 (4)
N1	0.0274 (2)	0.3344 (2)	-0.0640 (1)	0.044 (1)
C15	-0.0096 (2)	0.3531 (3)	-0.1245 (2)	0.054 (1)
C16	0.0080 (3)	0.3003 (4)	-0.1825 (2)	0.071 (2)
C17	0.0643 (3)	0.2284 (4)	-0.1766 (2)	0.081 (2)
C18	0.1050 (3)	0.2089 (3)	-0.1161 (2)	0.064 (2)
C19	0.0837 (2)	0.2639 (2)	-0.0593 (2)	0.043 (1)
N2	0.0843 (2)	0.3048 (2)	0.0583 (1)	0.043 (1)
C20	0.1102 (3)	0.2954 (3)	0.1233 (2)	0.051 (1)
C21	0.1695 (3)	0.2302 (3)	0.1428 (2)	0.068 (2)
C22	0.2037 (3)	0.1727 (3)	0.0928 (3)	0.079 (2)
C23	0.1775 (3)	0.1795 (3)	0.0272 (2)	0.063 (2)
C24	0.1167 (2)	0.2486 (2)	0.0095 (2)	0.044 (1)

$^a U_{eq} = \frac{1}{3}\sum U_{ii}$.
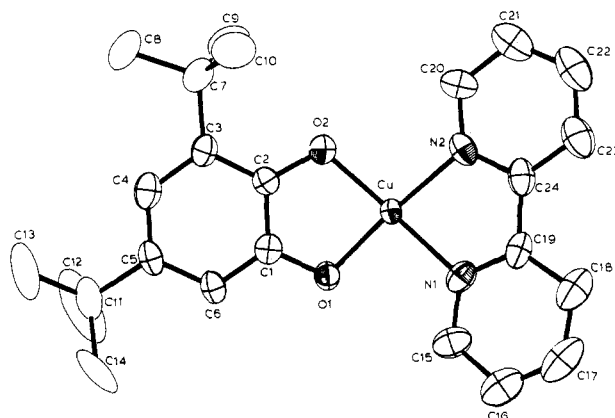
Figure 1. ORTEP drawing of the Cu(bpy)(DBCat) monomer showing the atom-numbering scheme used in both structure determinations.
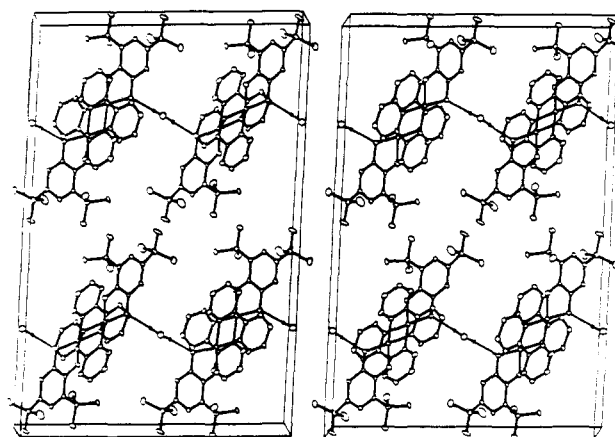
Figure 2. Stereoview showing intermolecular interactions between Cu(bpy)(DBCat) complex molecules through stacks in the crystal structure and hydrogen bonds with the water solvate molecule. This view is down the crystallographic 2-fold axis of the space group.
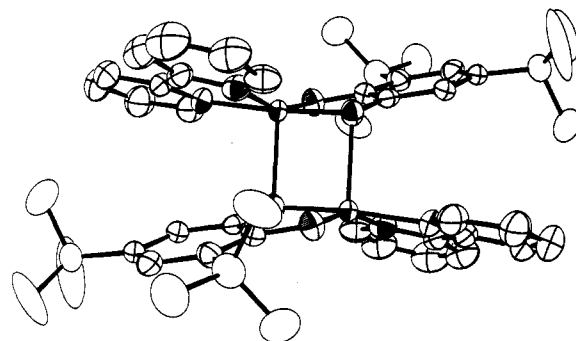
Table V. Bond Lengths (Å) and Selected Angles (deg) for
Cu(bpy)(DBCat)·0.5H$_2$O·1.5CH$_2$Cl$_2$[a]

Cu Coordination

Lengths

Cu–O1	1.901 (5)	Cu–N1	1.993 (6)
Cu–O2	1.870 (5)	Cu–N2	1.999 (6)

Angles

O1–Cu–O2	88.7 (2)	O2–Cu–N1	171.6 (2)
O1–Cu–N1	97.2 (2)	O2–Cu–N2	93.2 (2)
O1–Cu–N2	176.6 (2)	N1–Cu–N2	81.3 (2)

Catecholate

Lengths

O1–C1	1.364 (8)	C5–C11	1.534 (10)
O2–C2	1.338 (8)	C6–C1	1.407 (10)
C1–C2	1.407 (10)	C7–C8	1.525 (13)
C2–C3	1.418 (9)	C7–C9	1.530 (14)
C3–C4	1.396 (10)	C7–C10	1.549 (14)
C3–C7	1.535 (10)	C11–C12	1.543 (14)
C4–C5	1.379 (10)	C11–C13	1.557 (15)
C5–C6	1.382 (10)	C11–C14	1.518 (15)

Angles

Cu–O1–C1	106.8 (4)	O1–C1–C2	117.3 (6)
Cu–O2–C2	109.3 (4)	O2–C2–C1	116.5 (6)
O1–C1–C6	122.3 (7)	O2–C2–C3	124.0 (7)

Bipyridyl

Lengths

N1–C15	1.314 (9)	N2–C20	1.335 (9)
N1–C19	1.364 (8)	N2–C24	1.343 (8)
C15–C16	1.364 (10)	C20–C21	1.335 (9)
C16–C17	1.391 (12)	C21–C22	1.374 (10)
C17–C18	1.364 (12)	C22–C23	1.367 (12)
C18–C19	1.390 (10)	C23–C24	1.405 (10)
C19–C24	1.451 (10)		

Angles

Cu–N1–C19	113.6 (5)	Cu–N2–C24	114.7 (5)
Cu–N1–C15	127.9 (6)	Cu–N2–C20	125.0 (5)

Intermolecular Contacts

O1–O3	2.93 (1)	C1--C17′	3.16 (1)
C2--C17′	3.29 (1)	Cu--C16′	3.328 (7)
Cu--Cu′	8.296 (6)		

[a] A prime denotes atoms of the molecule generated by crystallographic inversion.

Figure 3. ORTEP drawing of the [Cu(bpy)(DBCat)]$_2$ dimer.

Table VI. Bond Lengths (Å) and Selected Angles (deg) for
[Cu(bpy)(DBCat)]$_2$[a]

Cu Coordination

Lengths

Cu–O1	1.908 (2)	Cu–N2	1.996 (3)
Cu–O2	1.909 (2)	Cu–O1′	2.330 (2)
Cu–N1	2.018 (3)	Cu--Cu′	3.0742 (8)

Angles

O1–Cu–O2	87.3 (1)	O2–Cu–N1	159.2 (1)
O1–Cu–N2	172.8 (1)	O2–Cu–O1′	104.4 (1)
O1–Cu–N1	94.5 (1)	N1–Cu–N2	79.8 (1)
O1–Cu–O1′	87.5 (1)	N2–Cu–O1′	97.5 (1)
O2–Cu–N2	96.3 (1)	N1–Cu–O1′	96.4 (1)

Catecholate

Lengths

O1–C1	1.354 (4)	C5–C11	1.514 (5)
O2–C2	1.350 (5)	C1–C6	1.383 (5)
C1–C2	1.409 (4)	C7–C8	1.526 (5)
C2–C3	1.408 (5)	C7–C9	1.535 (5)
C3–C4	1.390 (5)	C7–C10	1.506 (6)
C3–C7	1.535 (5)	C11–C12	1.497 (7)
C4–C5	1.392 (5)	C11–C13	1.520 (7)
C5–C6	1.398 (5)	C11–C14	1.563 (8)

Angles

Cu–O1–Cu′	92.5 (1)	O1–C1–C6	121.5 (3)
Cu–O1–C1	108.5 (2)	O1–C1–C2	117.4 (3)
Cu′–O1–C1	112.1 (2)	O2–C2–C1	116.6 (3)
Cu–O2–C2	109.0 (2)	O2–C2–C3	124.6 (3)

Bipyridyl

Lengths

N1–C15	1.339 (5)	N2–C20	1.335 (4)
N1–C19	1.341 (4)	N2–C24	1.342 (4)
C15–C16	1.383 (6)	C20–C21	1.368 (5)
C16–C17	1.358 (7)	C21–C22	1.378 (6)
C17–C18	1.368 (6)	C22–C23	1.345 (6)
C18–C19	1.393 (5)	C23–C24	1.413 (5)
C19–C24	1.451 (5)		

Angles

Cu–N1–C19	115.2 (2)	Cu–N2–C24	115.3 (2)
Cu–N1–C15	125.0 (3)	Cu–N2–C20	125.0 (2)

[a] A prime denotes atoms of the dimer generated by the crystallographic inversion operation.

2). These bond lengths compare well with values that range from 1.87 to 1.93 Å in bis(salicylaldehydato)copper(II),[14] bis(tropolonato)copper(II),[15] and bis(acetylacetonato)copper(II).[16] The Cu–N lengths are 1.993 (6) and 1.999 (6) Å, values which are slightly longer than usual Cu–N lengths, probably reflecting the strong donor character of the catecholate oxygen atoms. Carbon–oxygen lengths of the catecholate ligand are 1.364 (8) and 1.338 (8) Å, consistent with values found in other catecholate complexes. The longest of these lengths is to O1. Other C–C and C–N lengths and bond angles agree well with values obtained for di-*tert*-butylcatecholate and bipyridine ligands in previous structure determinations.

The water solvate molecule is located on the 2-fold axis of the space group, hydrogen bonded to oxygen atoms of two related complex molecules as shown in Figure 2. The separation between the water oxygen atom and O1 atoms of adjacent complex molecules is 2.93 (1) Å, typical of a normal hydrogen-bonding interaction. A ligand oxygen–water oxygen separation of 2.834 (2) Å has been reported for the hydrated copper oxalate complex Na$_2$Cu(C$_2$O$_4$)$_2$·2H$_2$O.[17]

As can also be seen in Figure 2, the Cu(bpy) regions of adjacent complex molecules related by a crystallographic inversion center form a stacking arrangement. Closest intermolecular contacts are between the catecholate chelate ring of one molecule and the bipyridyl ring containing N1. The shortest separation is between C1 and C17′ of adjacent molecules with a distance of 3.16 (1) Å, and the closest Cu–Cu separation is 8.296 (6) Å through the inversion center. Other short contacts are given in Table V.

Structural Features of the Cu(O$_2$C$_6$H$_2$(t-Bu)$_2$)(N$_2$C$_{10}$H$_8$) Dimer. The form of Cu(bpy)(DBCat) obtained from preparations carried out by using a limited amount of water or under anhydrous conditions is dimeric and unsolvated. The complex molecule

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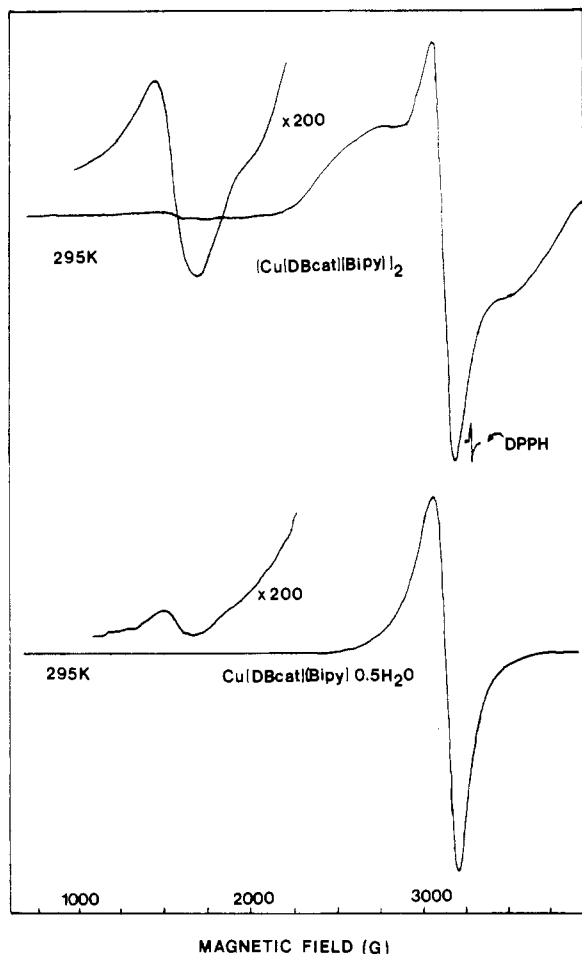
Figure 4. X-band EPR spectra recorded on powdered crystalline samples of dimeric [Cu(bpy)(DBCat)]$_2$ and monomeric Cu(bpy)(DBCat)·0.5H$_2$O·1.5CH$_2$Cl$_2$.

crystallizes as a centrosymmetric dimer in an orthorhombic space group. A view of the molecule is shown in Figure 3 and bond lengths and angles are given in Table VI. The metal atoms are five-coordinate and square pyramidal, with oxygen atoms of adjacent units bridging metals at apical coordination sites. The bridging oxygen atom is located at the 1-position of the 3,5-di-*tert*-butylcatechol ring, the same atom hydrogen bonded to the water molecule in the previous structure and the atom commonly found to bridge metals in dimeric complexes of this ligand.

The metal ion of [Cu(bpy)(DBCat)]$_2$ is displaced 0.216 Å from the basal plane of the complex. Both the catecholate and the bipyridine ligands are bent out of the N$_2$O$_2$ plane, away from the adjacent complex unit, by 19.7° for the catecholate plane and 13.5° for the bipyridine. The Cu–Cu distance in the dimer is 3.0742 (8) Å. Copper–oxygen lengths in the basal plane are 1.908 (2) and 1.909 (2) Å, and Cu–N lengths are 1.996 (3) and 2.018 (3) Å to N2 and N1. The Cu–O length at the apical site is 2.330 (2) Å, relatively short for bridging bonds in dimeric square-pyramidal complexes of copper. A value of 2.43 Å has been reported for the bis(dimethylglyoximato)copper(II) dimer.[18] The bis(8-hydroxyquinolinato)copper(II) dimer has a considerably longer bridge of 2.85 Å,[19] but the phenolate bridge in [Cu(en)(OPh)$_2$]$_2$ is more comparable with a value of 2.265 (4) Å.[20] As in the previous structure C–O lengths are typical of catecholate coordination with values of 1.353 (4) and 1.359 (4) Å, and other distances and angles in the ligands are typical of values found in other structure determinations.
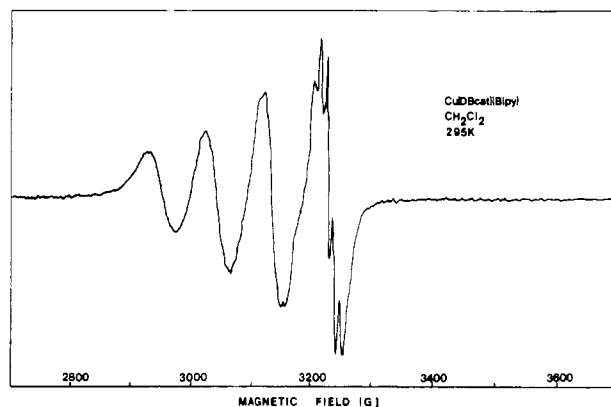
Figure 5. Solution EPR spectrum of Cu(bpy)(DBCat) recorded in CH$_2$Cl$_2$ at room temperature.
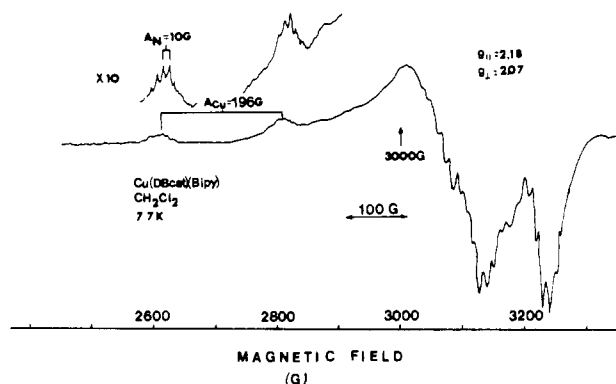
Figure 6. EPR spectrum of Cu(bpy)(DBCat) recorded in CH$_2$Cl$_2$ at 77 K.

EPR Spectra of Copper–Catecholate and Copper–Semiquinone Complexes. Magnetic measurements made on the monomeric and dimeric forms of Cu(bpy)(DBCat) gave values of 1.80 and 1.85 μ_B, respectively, values that are typical of $S = {}^1/_2$ Cu^{2+}. X-Band EPR spectra recorded on ground crystalline samples of *both* complexes show evidence of magnetic exchange between metal centers. Spectra for the two forms of the complex, shown in Figure 4, are quite different in appearance, with parallel and perpendicular signals unresolved at X-band frequencies. Both spectra show half-field signals near 1550 G, which are associated with $\Delta M_s = 2$ transitions arising from coupling between $S = {}^1/_2$ metal ions. Two potential mechanisms for exchange can be inferred from the solid-state structure of Cu(bpy)(DBCat)·0.5H$_2$O·1.5CH$_2$Cl$_2$. Exchange through hydrogen-bonding interactions has been observed previously for nominally monomeric Cu^{2+} complexes. However, in this case, since the water solvate bridges two complex molecules, exchange must occur through two hydrogen bonds. The second exchange mechanism would involve coupling through the charge-transfer pairing between bipyridine regions of complex molecules. A coupling mechanism of this type appears important in the magnetic properties of the 9,10-phenanthrenesemiquinone complex of ferric iron, Fe(phenSQ)$_3$.[21] At this point, discrimination between these two mechanisms is not possible, and it is likely that both contribute to the exchange interaction in some measure. The powder EPR spectrum of [Cu(bpy)(DBCat)]$_2$ shows features associated with the distorted square-pyramidal geometry about the metal. The half-field transition occurrs at 1540 G, and a zero-field splitting parameter, D, of 38 × 10^{-3} cm^{-1} can be estimated from this value.

At room temperature, solution spectra recorded on either the dimeric or monomeric forms of the complex in CH$_2$Cl$_2$ or in a CH$_2$Cl$_2$/C$_6$H$_5$CH$_3$ mixture show a four-line pattern ($g_{av} = 2.10$,

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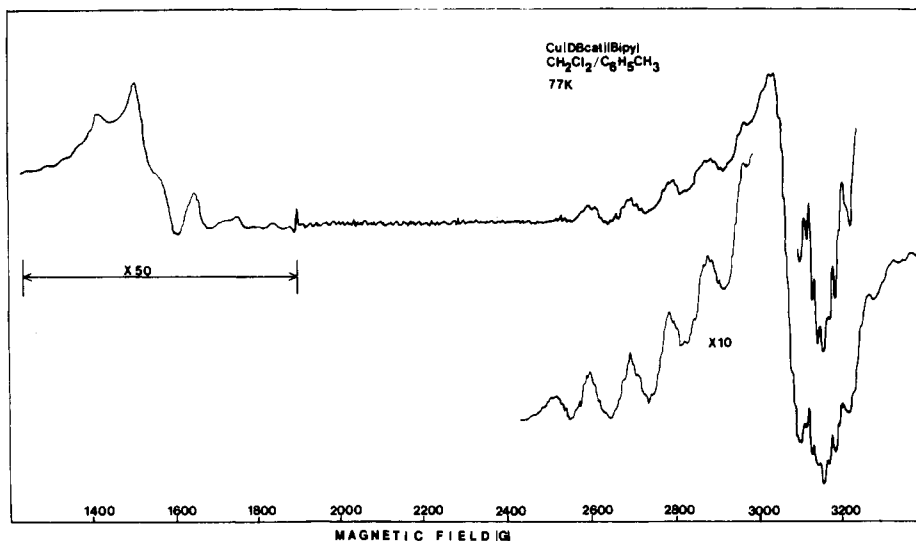
Figure 7. EPR spectrum of Cu(bpy)(DBCat) recorded in a 1:10 $CH_2Cl_2/C_6H_5CH_3$ glass at 77 K.
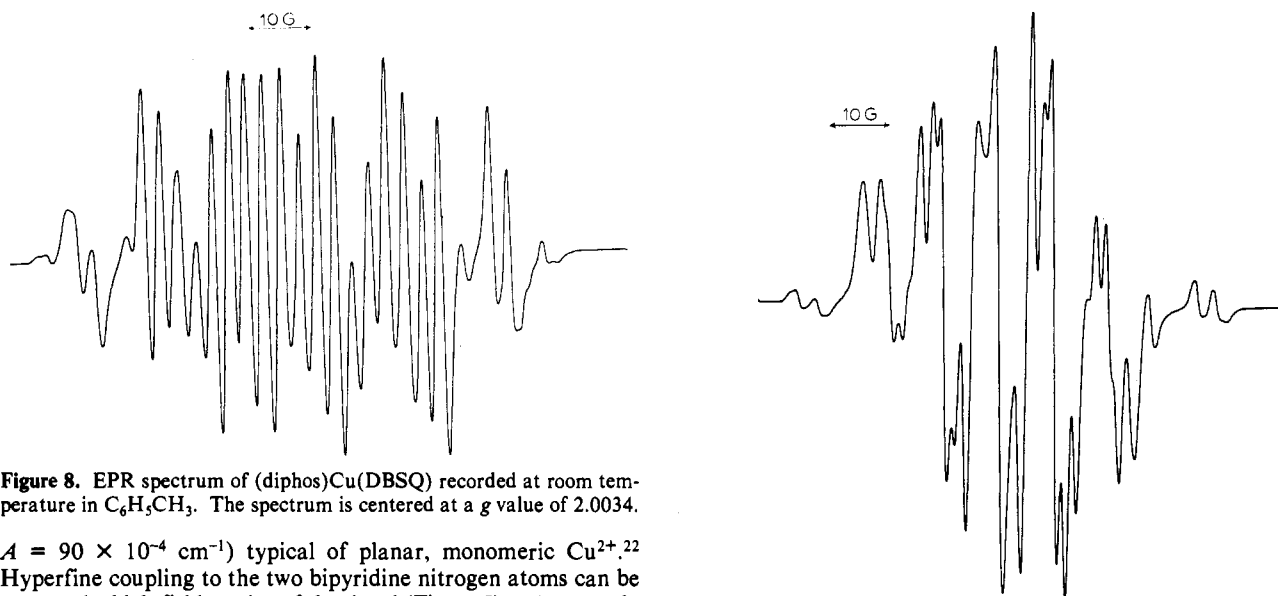

Figure 8. EPR spectrum of (diphos)Cu(DBSQ) recorded at room temperature in $C_6H_5CH_3$. The spectrum is centered at a *g* value of 2.0034.

$A = 90 \times 10^{-4}$ cm^{-1}) typical of planar, monomeric Cu^{2+}.[22] Hyperfine coupling to the two bipyridine nitrogen atoms can be seen on the high-field portion of the signal (Figure 5). . Apparently the complex exists in the monomeric form in noncoordinating solvents at room temperature. A solvent dependence is observed upon lowering the temperature of the solution to 77 K. In CH_2Cl_2 both forms of the complex give the spectrum shown in Figure 6, consistent with a monomeric structure ($g_\parallel$ = 2.18, $g_\perp$ = 2.07, $A_\parallel$ = 202 × 10^{-4} cm^{-1}). No half-field signal is observed, and nitrogen coupling can be observed on the perpendicular component. When a 1:10 $CH_2Cl_2/C_6H_5CH_3$ solvent mixture is used the 77 K spectrum shows evidence of exchange between metal ions (Figure 7). A seven-line coupling pattern is observed for $g_\parallel$ with $A_\parallel$ = 96 × 10^{-4} cm^{-1}, nearly half the value found for the monomer. This seven-line pattern arising from Cu–Cu coupling can also be observed on the half-field resonance, which is centered at 1570 G and shows an average spacing of 86 G.

Razuvaev has reported EPR spectra for di-*tert*-butylquinone complexes of copper that contain as counterligands phosphines, CO, acetylenes, and olefins.[23] These spectra are considerably different from those reported here and are essentially spectra of complexed semiquinone ligands. We have recorded and simulated the spectrum of (PPh$_3$)$_2$Cu(DBSQ). The spectrum is centered about an isotropic *g* value of 2.0032, and coupling constants of 10.o G to Cu, 15.5 G to two P atoms, and 2.75 G to the quinone

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Figure 9. EPR spectrum of (Ph$_2$P(CH$_2$CH$_2$C$_6$H$_4$N))Cu(DBSQ) in toluene. The spectrum is centered about a *g* value of 2.0028.

proton at the 4-position of the ring were used in the simulation. These values are similar to those reported by Razuvaev. The spectrum of (diphos)Cu(DBSQ), prepared by using procedures similar to those of Razuvaev, is shown in Figure 8. There is a clear shift in charge distribution with the softer donor phosphine ligands and, with the preference of Cu(I) for a tetrahedral geometry, a change in coordination geometry. To further study this effect two complexes containing phosphorus–nitrogen donor ligands were prepared. Ligands used were the iminophosphine ligand (I) prepared by Rauchfuss[13] and 2-[2-(diphenylphosphino)ethyl]-pyridine (II). In both cases the complexes were of the form

I

II
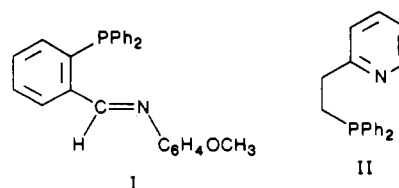
(P–N)Cu(DBSQ), similar to phosphine analogues. The spectrum of (Ph$_2$P(CH$_2$)$_2$py)Cu(DBSQ) is shown in Figure 9, but we have not succeeded in analyzing it in terms of component coupling constants. Monophosphine complexes like (PPh$_3$)Cu(DBSQ) have been noted by Razuvaev, and it is possible that the N-donor portion

of the ligand is uncoordinated in these complexes. However, spectra of the P–N complexes are quite different from spectra obtained on complexes prepared with monodentate and bidentate phosphine ligands.

Discussion

The structural and magnetic properties of (bpy)Cu(DBCat) clearly are consistent with a charge distribution assignment of the metal as Cu(II) and the quinone ligand as a catecholate. The possibility of a dimeric structure for the complex had not been considered in spectral[24] and electrochemical[25] studies. In particular, it may explain the two-electron-oxidation reaction reported by Sawyer.[25] EPR spectra recorded on related complexes with phosphorus and phosphorus–nitrogen donor ligands indicate a shift in charge distribution to Cu(I)–semiquinone. The counterligand dependence of the charge distribution in the Cu–quinone chelate ring raises a question about the possibility of a Cu^{I}SQ/Cu^{II}Cat solution equilibrium for Cu(bpy)(DBCat), similar to the cobalt and manganese examples[4,5] and the effect this might have on the chemical properties of the complex. A review of Brown's publications describing the chemical properties of the (N–N)Cu(Cat) complexes shows reactive patterns that are more common to Cu(I) species than Cu(II). Oxidation of the catechol ligand described in eq 1 occurs by O₂ attack at the metal[9] in a mechanism different

from that found by Rogic for a Cu(II) system which requires oxygen for oxidation of Cu(I) in the catalytic cycle.[8] Also quite characteristic of Cu(I) is the reactivity of (bpy)Cu(DBCat) and (phen)Cu(DBCat) toward C–Cl bonds.[26] Treatment of these complexes with CCl₄ gives (N–N)CuCl₂ and organic products in the absence of oxygen, and the reaction is accelerated in the presence of O₂. The observation that the potassium salt of DBCat fails to react with CCl₄ points to the necessity of the Cu ion. This chemistry is similar to that of Cu(I)–phenoxide complexes and uncharacteristic of Cu(II) complexes.

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Synthesis and IR, UV, NMR (¹H and ¹¹B), and Mass Spectral Studies of New β-Ketoamine Complexes of Boron: Crystal and Molecular Structure of OC₆H₄OBOC(R)CHC(R′)NR″ (R = p-ClC₆H₄, R′ = C₆H₅, R″ = CH₃)

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Twelve new β-ketoamine complexes of boron have been synthesized and assigned tetrahedral geometry by their IR, UV, and NMR (¹H, ¹¹B) spectral and other physicochemical measurements. The mass spectrum of OC₆H₄OBOC(CH₃)CHC(CH₃)NCH₃ is interpreted. OC₆H₄OBOC(R)CHC(R′)NR″ (R = p-ClC₆H₄, R′ = C₆H₅, R″ = CH₃) crystallizes in the triclinic space group P1̄ with a = 8.577 (4) Å, b = 10.656 (5) Å, c = 11.598 (5) Å, α = 84.77 (4)°, β = 83.25 (4)°, γ = 67.38 (4)°, and D$_c$ = 1.33 g cm⁻³ for two molecules per unit cell. The structure has been refined to R = 0.088 for 864 reflections. Each boron atom is bonded to one catechol and one β-ketoamine moiety. The tetrahedral environment around the boron atom is made up of two oxygen atoms from the catechol and an oxygen and a nitrogen atom from the β-ketoamine ligand.

Introduction

Examples of tetrahedral boron compounds with organic ligands such as catechol and β-ketoamines are limited in number,[2–4] and none of these have been characterized crystallographically. In our earlier studies with amino alcohol/phenol derivatives of boron,[5,6] we observe that the alkoxyboranes and 2-alkoxy-1,3,2-benzodioxaborole react with hydroxyl but not with amino protons.

The derivatives Ph₂BOCH₂CH₂NH₂,[7] (p-CH₃C₆H₄)₂-BOCH₂CH₂NH₂, and Ph₂BOCH₂CH₂CH₂NH₂[8] have been shown to be tetrahedral by X-ray crystallographic studies. A detailed study of F₂B(acac), Ph₂B(acac), and OC₆H₄OB(acac) (acac = acetylacetonate anion) by ¹H and ¹³C NMR spectroscopy[9,10] indicated delocalization of electrons in the β-diketonate ring, and this has been confirmed by X-ray crystal structure of F₂B(bzac)[11] (bzac = benzoylacetone anion) and (OAC)₂B(acac).[12]

The IR and ¹H NMR spectra of OC₆H₄OBN(H)C(C₆H₅)CH-

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