4860 *Inorg. Chem.* **1997,** *36,* 4860−4865

Pocket Semiquinonate Complexes of Cobalt(II), Copper(II), and Zinc(II) Prepared with the Hydrotris(cumenylmethylpyrazolyl)borate Ligand

Michael Ruf, Bruce C. Noll, Markus D. Groner, Gordon T. Yee, and Cortlandt G. Pierpont*

Department of Chemistry and Biochemistry, University of Colorado, Boulder, Colorado 80309

Received February 28, 1997[⊗]

3,5-Di-*tert*-butyl-1,2-semiquinonate (3,5-DBSQ) complexes of Co(II), Cu(II), and Zn(II) have been prepared that contain the hydrotris(cumenylmethyl-pyrazolyl)borate (Tp$^{\mathrm{Cum,Me}}$) coligand. Tp$^{\mathrm{Cum,Me}}$Zn(3,5-DBSQ) and Tp$^{\mathrm{Cum,Me}}$Cu(3,5-DBSQ) were prepared by treating the parent hydroxide, Tp$^{\mathrm{Cum,Me}}$M(OH), M = Cu and Zn, with 3,5-di-*tert*-butylcatechol. Tp$^{\mathrm{Cum,Me}}$Co(3,5-DBSQ) was prepared by a reaction between (Tp$^{\mathrm{Cum,Me}}$)$_2$Co and 3,5-DBCat. The identity of (Tp$^{\mathrm{Cum,Me}}$)$_2$Co in this reaction was confirmed by a structure determination [(Tp$^{\mathrm{Cum,Me}}$)$_2$Co: orthorhombic, *Pbcn*, $a = 17.7189(4)$ Å, $b = 17.4806(3)$ Å, $c = 25.7123(6)$ Å, $V = 7964.1(3)$ Å^3, $Z = 4$, $R(F) = 0.054$]. Intersecting cumenyl substituents of the pyrazolylborate ligand encapsulate the Co(II) ion. Structural characterization on all three members of the Tp$^{\mathrm{Cum,Me}}$M(3,5-DBSQ) series has been carried out. The complexes of Co(II) and Zn(II) are isomorphous and isostructural [Tp$^{\mathrm{Cum,Me}}$Co(3,5-DBSQ): triclinic, $P\bar{1}$, $a = 14.4631(2)$ Å, $b = 18.5438(3)$ Å, $c = 21.6142(2)$ Å, $\alpha = 79.8430(10)°$, $\beta = 90.0900(10)°$, $\gamma = 84.9900(10)°$, $V = 5683.45(13)$ Å^3, $Z = 4$, $R(F) = 0.072$; Tp$^{\mathrm{Cum,Me}}$Zn(3,5-DBSQ), triclinic, $P\bar{1}$, $a = 14.261(3)$ Å, $b = 18.760(7)$ Å, $c = 21.710(4)$ Å, $\alpha = 80.049(12)°$, $\beta = 89.853(8)°$, $\gamma = 85.542(12)°$, $V = 5703(3)$ Å^3, $Z = 4$, $R(F) = 0.064$]. Tp$^{\mathrm{Cum,Me}}$Cu(3,5-DBSQ) [monoclinic, $P2_1/c$, $a = 19.3081(3)$ Å, $b = 13.0291(2)$ Å, $c = 21.4783(4)$ Å, $\beta = 102.8420(10)°$, $V = 5268.1(2)$ Å^3, $Z = 4$, $R(F) = 0.071$] has a distorted square pyramidal structure, the complexes of Zn and Co have structures that are closer to a trigonal bipyramid. Parent catecholate complexes of all three metals are unusually stable in air but undergo slow oxidation in solution to give the semiquinonate products characterized structurally. Copper(II) and SQ spins of Tp$^{\mathrm{Cum,Me}}$Cu(3,5-DBSQ) are located in orthogonal orbitals, and the complex has a $S = 1$ spin state. The charge distribution in Tp$^{\mathrm{Cum,Me}}$Co(3,5-DBSQ) is Co(II)−SQ, rather than the more common Co(III)−Cat, due to surprisingly weak donation by the Tp$^{\mathrm{Cum,Me}}$ nitrogens.

Introduction

Much of the coordination chemistry of catecholate and radical semiquinonate ligands has been concerned with electron transfer and magnetism.[1] Unless stabilized by strong π donation to an electron deficient metal ion, catecholate (Cat) ligands are strong reducing agents. Aerobic oxidation of coordinated catechol ligands may lead to oxidative cleavage of the aromatic ring by an inner-sphere mechanism that may involve a peroxysemiquinone intermediate.[2] Outer-sphere oxidation results in formation of a coordinated semiquinonate (SQ) ligand with partial dioxygen reduction to superoxide.[3] Aerobic oxidation of a parent catecholate complex is a convenient synthetic route to complexes containing SQ radical anions. Magnetic measurements have been used to study metal−SQ exchange for compounds containing paramagnetic metal ions and SQ−SQ exchange for compounds containing coupled radical ligands.[4] Valence tautomerism has been studied for complexes of Co and Mn as a special example of inner-sphere metal−ligand electron transfer.[5] These investigations have involved equilibria between redox isomers differing in the distribution of charge between metal and quinone ligand for the M$^{\mathrm{II}}$(N-N)(SQ)$_2$, M = Co and Mn, series.

Ruf and Vahrenkamp recently described the chemistry of Tp$^{\mathrm{Cum,Me}}$Zn(OH).[6] The hydroxo ligand of this complex is a strong base contained within a protective pocket created by the cumenyl substituents of the tris(pyrazolyl)borate ligand. This complex has been used to prepare Tp$^{\mathrm{Cum,Me}}$Zn(3,5-DBSQ) by reaction with H$_2$(3,5-DBCat). Similar synthetic procedures have been used to form Tp$^{\mathrm{Cum,Me}}$Cu(OH) and Tp$^{\mathrm{Cum,Me}}$Cu(3,5-DBSQ). The addition of K(Tp$^{\mathrm{Cum,Me}}$) to Co^{2+} has been found to give (Tp$^{\mathrm{Cum,Me}}$)$_2$Co, and this product has been used as a precursor to Tp$^{\mathrm{Cum,Me}}$Co(3,5-DBSQ). The quinone ligand of each of these compounds is encapsulated by the substituents of the Tp$^{\mathrm{Cum,Me}}$ ligand contributing to unique electronic and magnetic properties.

Experimental Section

Materials. 3,5-Di-*tert*-butylcatechol, H$_2$(3,5-DBCat), was purchased from Aldrich. K(Tp$^{\mathrm{Cum,Me}}$) and Tp$^{\mathrm{Cum,Me}}$Zn(OH) were prepared by procedures described by Ruf and Vahrenkamp.[6]

Tp$^{\mathrm{Cum,Me}}$Zn(3,5-DBSQ). Tp$^{\mathrm{Cum,Me}}$Zn(OH) (200 mg, 0.29 mmol) was dissolved in 50 mL of a 1:1 dichloromethane/methanol solution. H$_2$(3,5-DBCat) (64 mg, 0.29 mmol) was added, and the mixture was stirred for 30 min. The solution was initially colorless. After exposure to air for the period of 12 h the solution turned green, and dark green crystals formed. The crystals were separated from the solution by filtration and dried *in vacuo* to give 211 mg of Tp$^{\mathrm{Cum,Me}}$Zn(3,5-DBSQ) in 82% yield.

Tp$^{\mathrm{Cum,Me}}$Cu(OH). K(Tp$^{\mathrm{Cum,Me}}$) (1.00 g, 1.54 mmol) was dissolved in 100 mL of dichloromethane, and a methanol (50 mL) solution of Cu(ClO$_4$)$_2$·6 H$_2$O (571 mg, 1.54 mmol) was added. After stirring of the green reaction mixture for 15 min, KOH (86 mg, 1.54 mmol) was

---

[⊗] Abstract published in *Advance ACS Abstracts,* September 15, 1997.

(1) Pierpont, C. G.; Lange, C. W. *Prog. Inorg. Chem.* **1994**, *41*, 331.

(2) (a) Speier, G.; Tyeklár, Z.; Szabó, II, L; Tóth, P.; Pierpont, C. G.; Hendrickson, D. N. In *The Activation of Dioxygen and Homogeneous Catalytic Oxidation*; Barton, D. H. R., Martell, A. E., Sawyer, D. T., Eds.; Plenum: New York, 1993; p 423. (b) Barbaro, P.; Bianchini, C.; Linn, K.; Mealli, C.; Meli, A.; Vizza, F.; Laschi, F.; Zanello, P. *Inorg. Chim. Acta* **1992**, *198−200*, 31.

(3) Hubbard, C. D.; Gerhard, A.; van Eldik, R. *Inorg. Chem.* **1991**, *30*, 5023.

(4) (a) Attia, A. S.; Conklin, B. J.; Lange, C. W.; Pierpont, C. G. *Inorg. Chem.* **1996**, *35*, 1033. (b) Lange, C. W.; Conklin, B. J.; Pierpont, C. G. *Inorg. Chem.* **1994**, *33*, 1276.

(5) (a) Jung, O.-S.; Jo, D. H.; Lee, Y.-A; Conklin, B. J.; Pierpont, C. G. *Inorg. Chem.* **1997**, *36*, 19. (b) Attia, A. S.; Pierpont, C. G. *Inorg. Chem.* **1995**, *34*, 1172.

(6) Ruf, M.; Vahrenkamp, H. *Inorg. Chem.* **1996**, *35*, 6571.

Table 1. Crystallographic Data for ($Tp^{Cum,Me}$)Zn(3,5-DBSQ), ($Tp^{Cum,Me}$)Cu(3,5-DBSQ), ($Tp^{Cum,Me}$)Co(3,5-DBSQ), and $(Tp^{Cum,Me})_2Co$

	$Tp^{Cum,Me}$Zn(3,5DBSQ)	$Tp^{Cum,Me}$Co(3,5DBSQ)	$Tp^{Cum,Me}$Cu(3,5DBSQ)	$(Tp^{Cum,Me})_2$Co
empirical formula	$C_{106}H_{132}B_2N_{12}O_4Zn_2\cdot 4CH_2Cl_2$	$C_{106}H_{132}B_2N_{12}O_4Co_2\cdot 4CH_2Cl_2$	$C_{53}H_{66}BCuN_6O_2$	$C_{78}H_{92}B_2CoN_2\cdot 2.5CH_2Cl_2\cdot 0.5CH_3CN$
formula mass	2130.30	2117.42	893.47	1508.50
crystsystem	triclinic	triclinic	monoclinic	orthorhombic
space group	$P\bar{1}$	$P\bar{1}$	$P2_1/c$	*Pbcn*
a (Å)	14.261(3)	14.4631(2)	19.3081(3)	17.7189(4)
b (Å)	18.760(7)	18.5438(3)	13.0291(2)	17.4806(3)
c (Å)	21.710(4)	21.6142(2)	21.4783(4)	25.7123(6)
α (deg)	80.049(12)	79.8430(10)	90	90
β (deg)	89.853(8)	90.0900(10)	102.8420(10)	90
γ (deg)	85.542(12)	84.9900(10)	90	90
V (Å^3)	5703(3)	5683.45(13)	5268.1(2)	7964.1(3)
Z	2	2	4	4
ρ_{calc} (g·cm^{-3})	1.241	1.237	1.127	1.258
μ (mm^{-1})	0.662	0.534	0.457	0.435
transm coeff	0.86 and 0.73	0.924 and 0.303	0.93 and 0.76	0.83 and 0.75
T (K)	145(2)	146(2)	293(2)	148(2)
λ, Å	0.710 73 (Mo Kα)	0.710 73 (Mo Kα)	0.710 73 (Mo Kα)	0.710 73 (Mo Kα)
reflcns collcd	39 839	52 236	45 805	50 964
unique reflcns	26 114 (R(int) = 0.022)	22 050 (R(int) = 0.121)	9263 (R(int) = 0.107)	9817 (R(int) = 0.0261)
reflcns obsd	21409	11517	4945	8203
R index[1] [$I > 2\sigma(I)$]	$R1 = 0.0644$	$R1 = 0.0720$	$R1 = 0.0707$	$R1 = 0.0538$
R indices[a] (all data)	$R1 = 0.0816$, w$R2 = 0.1739$	w$R2 = 0.2011$	w$R2 = 0.2146$	w$R2 = 0.1577$

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$; w$R2 = \{\sum[w(F_o{}^2 - F_c{}^2)^2]/\sum[w(F_o{}^2)^2]\}^{1/2}$.

added to complete the precipitation of $KClO_4$. After the mixture was stirred for 2 h, colorless $KClO_4$ was separated from the green solution by filtration, and the volume of the solution was reduced to 50 mL under vacuum. A green microcrystalline solid formed. It was separated from the solution by filtration, washed with small quantities of methanol, and dried *in vacuo*. $Tp^{Cum,Me}$Cu(OH) was obtained in 61% yield (650 mg).

$Tp^{Cum,Me}$Cu(3,5-DBSQ). $Tp^{Cum,Me}$Cu(OH) (200 mg, 0.29 mmol) and H_2(3,5-DBCat) (64 mg, 0.29 mmol) were combined using the procedures described for the formation of $Tp^{Cum,Me}$Zn(3,5-DBSQ). Air oxidation of the catecholate complex formed initially in the procedure gave $Tp^{Cum,Me}$Cu(3,5-DBSQ) in 67% yield (174 mg).

$(Tp^{Cum,Me})_2$Co. K($Tp^{Cum,Me}$) (1.00 g, 1.54 mmol) was dissolved in 100 mL of dichloromethane, and a methanol (50 mL) solution of Co($ClO_4)_2\cdot 6H_2O$ (282 mg, 0.71 mmol) was added. The pink solution was stirred for 2 h and a precipitate of colorless $KClO_4$ was separated by filtration. The volume of the solution was reduced to 50 mL under vacuum, and a pink precipitate formed. Microcrystalline $(Tp^{Cum,Me})_2$Co was isolated by filtration (438 mg, 44% yield), washed with small quantities of MeOH, and dried *in vacuo*. Crystals suitable for crystallographic characterization were grown by slow evaporation of a saturated dichloromethane/acetonitrile solution.

$Tp^{Cum,Me}$Co(3,5-DBSQ). $(Tp^{Cum,Me})_2$Co (200 mg, 0.16 mmol) dissolved in 50 mL dichloromethane and H_2(3,5-DBCat) (35 mg, 0.16 mmol) dissolved in 25 mL methanol were combined and stirred for 30 min. After sitting in air for 12 h the solution had turned green and dark green crystals of $Tp^{Cum,Me}$Co(3,5-DBSQ) had formed. The crystals were isolated by filtration and dried *in vacuo* to give 45 mg of $Tp^{Cum,Me}$Co(3,5-DBSQ) in 32% yield.

Physical Methods. Electronic spectra were recorded on a Perkin-Elmer Lambda 9 spectrophotometer. Infrared spectra were recorded on a Perkin-Elmer 1600 FTIR with samples prepared as KBr pellets. Magnetic measurements were made using a Quantum Design SQUID magnetometer at the NIST Laboratory, Boulder, CO. Cyclic voltammograms were obtained with a Cypress Systems Inc. computer-controlled electroanalysis system. A platinum working electrode was used. The Ag/Ag$^+$ reference electrode consisted of a CH_3CN solution of $AgPF_6$ in contact with a silver wire placed in glass tubing with a Vycor frit at one end to allow ion transport.

Crystallographic Structure Determination on $Tp^{Cum,Me}$Zn(3,5-DBSQ)·$2CH_2Cl_2$. Dark green crystals were obtained by slow evaporation of a saturated dichloromethane/methanol solution of the complex. A sphere of intensity data was collected at 145(2) K using a Siemens SMART system equipped with a CCD detector. Crystals were found to form in the triclinic crystal system, space group $P\bar{1}$, in a unit cell of the dimensions given in Table 1. The structure was solved using direct methods. A β angle close to 90° and a unit cell containing two independent complex molecules and four independent CH_2Cl_2 solvate molecules aroused suspicion about the choice of unit cell and crystal system. LePage's MISSYM routine of PLATON was used to search for undetected symmetry with a negative result.[7] Features of the independent $Tp^{Cum,Me}$Zn(3,5-DBSQ) complex molecules were compared with the result that differences in the rotational disposition of cumenyl substituents result in structural dissymmetry for the two molecules. Refinement of both independent complex molecules and the four solvate molecules converged with $R(F) = 0.064$ and $R_w(F^2) = 0.174$ for all independent data.

Crystallographic Structure Determination on $Tp^{Cum,Me}$Co(3,5-DBSQ)·$2CH_2Cl_2$. Dark green crystals were used for data collection and structure determination by following the procedure used for the Zn analog. Crystals of the two compounds are isomorphous, and the results of the structure determinations are similar. Unit cell dimensions are given in Table 1. Refinement of both independent complex molecules and the four solvate molecules converged with $R(F) = 0.072$ and $R_w(F^2) = 0.201$ for all independent data.

Crystallographic Structure Determination on $Tp^{Cum,Me}$Cu(3,5-DBSQ). Dark green crystals obtained under conditions that were used to form crystals of the Zn and Co analogs form in the monoclinic crystal system, space group $P2_1/c$. A sphere of data was collected at 293(2) K using a Siemens SMART system equipped with a CCD detector. Crystals of $Tp^{Cum,Me}$Cu(3,5-DBSQ) were found to be unsolvated. Unit cell dimensions are listed in Table 1 with other crystallographic parameters. Refinement of the complex molecule converged with $R(F) = 0.071$ and $R_w(F^2) = 0.155$ for all independent data.

Crystallographic Structure Determination on $(Tp^{Cum,Me})_2$Co·$2.5CH_2Cl_2\cdot 0.5CH_3CN$. Pink crystals were grown from a dichloromethane/acetonitrile solution. Data were collected at 148(2) K using a Siemens SMART system equipped with a CCD detector. Crystals form in the orthorhombic crystal system, space group *Pbcn*, with crystallographically imposed 2-fold symmetry for the complex molecule. The structure was solved using direct methods. A difference Fourier calculated with phases of the complex showed the locations of dichloromethane and acetonitrile molecules of crystallization. Refinement converged with $R(F) = 0.054$ and $R_w(F^2) = 0.158$ for all independent data.

Results and Discussion

The hydrotris(3-*p*-cumenyl-5-methylpyrazolyl)borate ligand ($Tp^{Cum,Me}$) was developed by Ruf and Vahrenkamp for studies

---

(7) Spek, A. L. *Acta Crystallogr., Sect A* **1990**, *A46*, C34.

on the hydrolytic cleavage of protic substrate molecules at an encapsulated pocket.[6,8] Reactions with Tp$^{\mathrm{Cum,Me}}$Zn(OH) show that the complex is a viable model for the active sites of hydrolytic zinc enzymes. Cumenyl substituents create a protected site at the metal that may accommodate small bidentate ligands, but exclude ligands of a specific size and shape. Catecholate ligands may fit into the pocket as a protective environment that might slow the rate of aerobic oxidation to semiquinone. Chelated semiquinonate ligands exhibit magnetic exchange with paramagnetic metal ions, but intermolecular exchange sometimes complicates interpretation of temperature-dependent magnetic measurements. The Tp$^{\mathrm{Cum,Me}}$ pocket may reduce intermolecular coupling and provide stereochemistry that will permit studies on spin orientation dependence. This is an important factor in determining the nature of exchange, ferromagnetic or antiferromagnetic, in simple multispin systems. Metal ions chosen for this investigation are the Zn, Cu, Co series, each for a specific interest that will be described below.

Tp$^{\mathrm{Cum,Me}}$Zn(3,5-DBSQ) and Outer-Sphere Cat/SQ Electron Transfer. Catecholate complexes of zinc are subject to aerobic oxidation by even trace quantities of dioxygen in an otherwise inert atmosphere.[9] This is easily observed with the rapid appearance of the green or blue-green semiquinonate from the colorless solution containing the parent catecholate complex. Aerobic catechol oxidation provides a useful route to semiquinonate radical complexes for studies on magnetic properties, and the contrast with complexes of d^0 Mo(VI) illustrates the importance of π donation effects in stabilizing catecholate coordination.[1]

The product formed initially from the reaction between Tp$^{\mathrm{Cum,Me}}$Zn(OH) and 3,5-DBCat remains colorless in solution for the period of 1 h after the reactants are combined. Deprotonation of H$_2$(3,5-DBCat) may take place stoichiometrically giving initially Tp$^{\mathrm{Cum,Me}}$Zn(H(3,5-DBCat)) as found in reactions with octahydroxyphthalocyanine.[10] Aerobic oxidation of the partially deprotonated catecholate ligand occurs slowly forming the semiquinonate product. Electrochemical characterization on Tp$^{\mathrm{Cum,Me}}$Zn(3,5-DBSQ), the green product obtained after the reaction mixture has been exposed to air for several hours, shows that the [Tp$^{\mathrm{Cum,Me}}$Zn(3,5-DBCat)]$^-$/Tp$^{\mathrm{Cum,Me}}$Zn(3,5-DBSQ) oxidation potential (Figure 1) appears at -1.10 V (vs Fc/Fc$^+$) (Table 2). Related complexes prepared with Co and Cu undergo oxidation at similar potentials, and the voltages have been confirmed by electrochemical characterization on solutions containing both the complex and a ferrocene reference. The crystal structure of Tp$^{\mathrm{Cum,Me}}$Zn(3,5-DBSQ) shown in Figure 2 shows that the 3,5-DBSQ ligand is encapsulated by cumenyl substituents of the Tp$^{\mathrm{Cum,Me}}$ ligand. Two cumenyl phenyl rings are located on either side of the plane of the quinone ligand and tipped away from the *tert*-butyl group at the 3-position of the quinone ligand. The third cumenyl ring and methyl groups of both *tert*-butyl groups block access from other sides. Isolation of the catecholate ligand in the hydrophobic pocket defined by the Tp$^{\mathrm{Cum,Me}}$ cumenyl and catechol *tert*-butyl substituents appears responsible for the slow rate of catecholate oxidation. Electron transfer must occur as a relatively slow outer-sphere process from within the pocket.

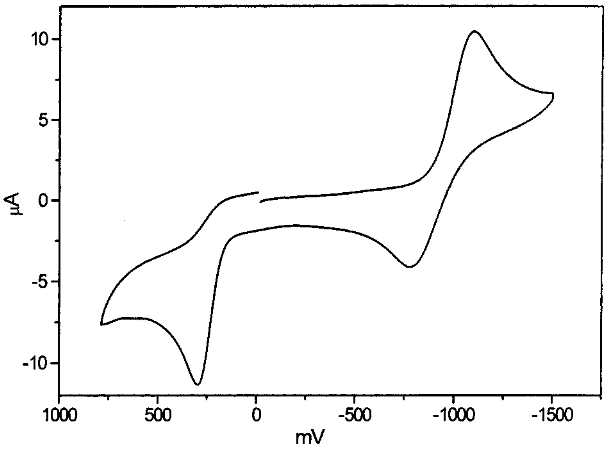

Figure 1. Cyclic voltammogram of (Tp$^{\mathrm{Cum,Me}}$)Co(3,5-DBSQ) recorded at a scan rate of 50 mV/s. The potential is referenced to the Ag/Ag$^+$ couple. At negative potential the [(Tp$^{\mathrm{Cum,Me}}$)Co(3,5-DBCat)]$^-$/(Tp$^{\mathrm{Cum,Me}}$)Co(3,5-DBSQ) couple is observed. Irreversible oxidation of the 3,5-DBSQ ligand appears at the positive potential. CV's of the Zn and Cu analogs have a similar appearance.

Table 2. Spectroscopic and Electrochemical Properties of (Tp$^{\mathrm{Cum,Me}}$)Zn(3,5-DBSQ), (Tp$^{\mathrm{Cum,Me}}$)Cu(3,5-DBSQ), and (Tp$^{\mathrm{Cum,Me}}$)Co(3,5-DBSQ)

compd	$\lambda_{\max}$ (nm, ϵ ($\times 10^{-3}$, M^{-1} cm^{-1}))	$E_{1/2}$, V^a (ΔE_p, mV)
(Tp$^{\mathrm{Cum,Me}}$)Zn(3,5-DBSQ)	312 (10.6), 774 (0.6)	0.07,^{b} -1.10 (230)
(Tp$^{\mathrm{Cum,Me}}$)Cu(3,5-DBSQ)	309 (10.2), 389 (1.2), 714 (0.6)	0.22, -0.99 (172)
(Tp$^{\mathrm{Cum,Me}}$)Co(3,5-DBSQ)	305 (9.5), 382 (6.8), 622 (0.6), 722 (0.7)	0.24, -1.12 (146)

^{a} $E_{1/2}$ values recorded at scan rates of 50 mV/s and referenced to the Fc/Fc$^+$ couple. ^{b} Ligand SQ/BQ oxidation appears irreversibly at the positive potential; the Cat/SQ couple appears at the negative potential.

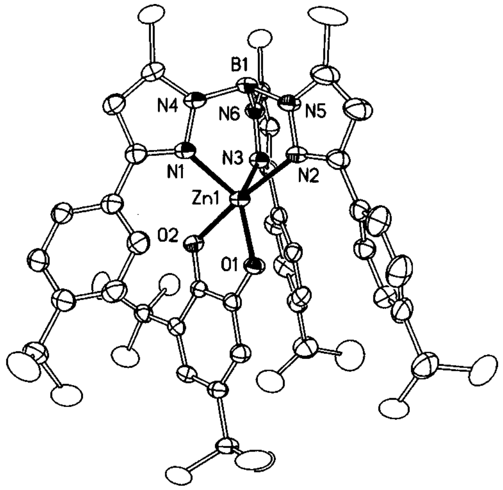

Figure 2. View of one of the independent (Tp$^{\mathrm{Cum,Me}}$)Zn(3,5-DBSQ) complex molecules.

Tp$^{\mathrm{Cum,Me}}$Cu(3,5-DBSQ) and Spin-Directed Cu−SQ Ferromagnetic Exchange. The coordination geometry of Tp$^{\mathrm{Cum,Me}}$Zn(3,5-DBSQ) is intermediate between trigonal bipyramidal (TBP) and square pyramidal (SP). Angles about the metal from N1 to O2, N2, and N3 are close to 90° (Table 3), and the N2−Zn−O2 angle of 172.56° is a reasonable *trans* angle. Semiquinone oxygen O1 is out of the plane that would define the base of a SP structure resulting in average angles of 126.7(1) and 136.6(1)° about the metal to the atoms shown as N1 and N3 in Figure 2. Five-coordinate complexes of Cu(II) composed of nitrogen and oxygen donor ligands typically have structures that are intermediate between TBP and SP but more closely resemble the SP geometry. Metal spin in these complexes is contained in the high-energy d-orbital of the basal plane. A

---

(8) (a) Ruf, M.; Burth, R.; Weis, K.; Vahrenkamp, H. *Chem. Ber.* **1996**, *129*, 1251. (b) Ruf, M.; Weis, K.; Brasack, I.; Vahrenkamp, H. *Inorg. Chim. Acta* **1996**, *250*, 271.

(9) Rhorscheid, F.; Balch, A.; Holm, R. *Inorg. Chem.* **1966**, *5*, 1542.

(10) Ruf, M.; Lawrence, A.; Noll, B.; Pierpont, C. G. Submitted for publication.

Table 3. Selected Bond Lengths and Angles for $(\mathrm{Tp^{Cum,Me}})$Zn(3,5-DBSQ), $(\mathrm{Tp^{Cum,Me}})$Cu(3,5-DBSQ), and $(\mathrm{Tp^{Cum,Me}})$Co(3,5-DBSQ)[a]

	$(\mathrm{Tp^{Cum,Me}})$-Zn(3,5-DBSQ)	$(\mathrm{Tp^{Cum,Me}})$-Cu(3,5-DBSQ)	$(\mathrm{Tp^{Cum,Me}})$-Co(3,5-DBSQ)
		Lengths (Å)	
M−O1	1.965(2)	1.952(3)	1.961(3)
M−O2	2.136(2)	1.971(3)	2.053(3)
M−N1	2.033(3)	2.239(4)	2.035(3)
M−N2	2.179(3)	1.993(4)	2.171(3)
M−N3	2.046(3)	1.982(4)	2.040(3)
C1−O1	1.288(4)	1.279(5)	1.301(5)
C2−O2	1.275(3)	1.265(6)	1.271(4)
C1−C2	1.469(4)	1.457(7)	1.461(5)
C2−C3	1.413(4)	1.409(7)	1.396(5)
C3−C4	1.373(4)	1.368(8)	1.359(5)
C4−C5	1.435(4)	1.434(8)	1.441(6)
C5−C6	1.371(5)	1.346(7)	1.377(5)
C1−C6	1.445(4)	1.437(7)	1.443(5)
		Angles (deg)	
O1−M−O2	80.06(8)	82.70(14)	80.86(10)
O2−M−N2	174.29(9)	176.93(15)	173.29(11)
O1−M−N1	126.75(10)	115.00(14)	125.84(11)
O1−M−N3	136.61(10)	151.59(15)	139.28(12)
N1−M−N3	96.40(10)	93.23(15)	94.84(12)
O1−M−N2	97.33(9)	95.63(15)	94.25(11)
O2−M−N1	95.45(9)	92.37(14)	97.70(12)
N1−M−N2	89.26(10)	90.68(15)	87.78(12)
N2−M−N3	86.07(10)	86.80(15)	84.83(12)

[a] Atoms labels are consistent with the figures. Values for M = Zn and Co are averaged for two crystallographically independent complex molecules.

radical semiquinone ligand chelated in the tetragonal plane of a SP Cu(II) complex would have its spin in a π orbital that is orthogonal to the σ metal spin. Chelation should result in strong ferromagnetic spin−spin exchange.

The precursor to $\mathrm{Tp^{Cum,Me}}$Cu(3,5-DBSQ) following the procedure used to form the Zn analog is $\mathrm{Tp^{Cum,Me}}$Cu(OH). Procedures used in the synthesis of $\mathrm{Tp^{Cum,Me}}$Zn(OH) were used to form $\mathrm{Tp^{Cum,Me}}$Cu(OH), and this complex was treated with 3,5-DBCat to give $\mathrm{Tp^{Cum,Me}}$Cu(3,5-DBSQ). The O−H stretching vibration of $\mathrm{Tp^{Cum,Me}}$Cu(OH) appears as a sharp band at 3642 cm^{-1}, similar to ν(O−H) of $\mathrm{Tp^{Cum,Me}}$Zn(OH) that appears at 3649 cm^{-1}.[6] This and other similarities in the IR spectra of the two compounds lead to the conclusion that the two compounds are isostructural with both containing the unusual terminal −OH ligand in the $\mathrm{Tp^{Cum,Me}}$ pocket. Structural features of $\mathrm{Tp^{Cum,Me}}$Cu(3,5-DBSQ) shown in Figure 3 do indeed show angles and bond lengths (Table 3) that reflect the shift to a square pyramidal geometry relative to $\mathrm{Tp^{Cum,Me}}$Zn(3,5-DBSQ). The location of the 3,5-DBSQ oxygen O1 is much closer to the O2, N2, N3 plane for $\mathrm{Tp^{Cum,Me}}$Cu(3,5-DBSQ) with bond angles to N1 and N3 of 115.0(1) and 151.6(2)°. The long apical Cu-N1 length (2.239(4) Å) is consistent with spin localization in the basal orbital interacting with N2, N3, O1, and O2.

The structure of $\mathrm{Tp^{Cum,Me}}$Cu(3,5-DBSQ) may be considered to be a distorted square pyramid with the 3,5-DBSQ ligand chelated in the tetragonal plane. Magnetic measurements recorded for the complex over the temperature range from 350 to 5 K (Figure 4) show that magnetic moment remains essentially constant at a value of 2.9−3.0 μ_B. Two noninteracting $S = {}^1/_2$ centers would give a combined magnetic moment of 2.45 μ_B, and antiferromagnetic coupling would result in a temperature dependent drop below this value. Ferromagnetic exchange to give a $S = 1$ spin state would result in a magnetic moment of 2.83 μB, slightly below the experimental value.

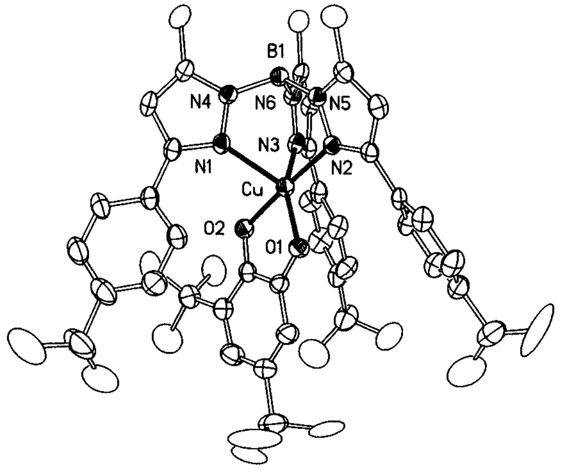

Figure 3. View of the $(\mathrm{Tp^{Cum,Me}})$Cu(3,5-DBSQ) complex molecule.

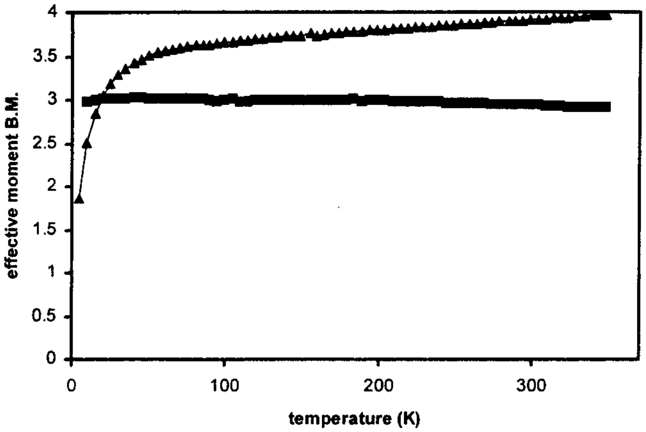

Figure 4. Temperature-dependent magnetic measurements on $(\mathrm{Tp^{Cum,Me}})$Cu(3,5-DBSQ) (■) and $(\mathrm{Tp^{Cum,Me}})$Co(3,5-DBSQ) (▲).

Cu−SQ magnetic exchange in $\mathrm{Tp^{Cum,Me}}$Cu(3,5-DBSQ) is strong and ferromagnetic. Copper(II) has been observed to couple ferromagnetically with organic radicals, but few of these complexes have been characterized structurally. Cu(TMP)$^+$ containing the tetramesitylporphyrin radical anion was observed to show a temperature-independent magnetic moment of 2.6 μ_B, a value attributed to ferromagnetic Cu^{2+}−radical exchange.[11] Cu(TPP)$^+$ shows the effects of antiferromagnetic exchange. Structural characterization indicated that ruffling of the TPP ring breaks the orthogonality of metal σ and porphyrin π orbitals, while the ring of Cu(TMP)$^+$ remains planar.[12] The Cu$^{\mathrm{II}}$−tyrosyl radical center of galactose oxidase is reported to be coupled antiferromagnetically.[13] The results of structural characterization indicate that the plane of the radical is twisted out of the basal plane of the square pyramidal Cu(II) complex.[14] Dei and Gatteschi have reported ferromagnetic Cu(II)−SQ exchange for [Cu(Me$_3$[12]N$_3$)(3,5-DBSQ)](ClO$_4$), a complex that is probably similar in coordination geometry to $\mathrm{Tp^{Cum,Me}}$Cu(3,5-DBSQ).[15] Ferromagnetic exchange has also been reported for Cu(py)$_2$(Cat-N−SQ), where magnetic moment was found to be 2.85 μ_B and the planar tridentate Cat-N−SQ^{2-} radical occupies basal coordination sites.[16]

---

(11) Song, H.; Reed, C. A.; Scheidt, W. R. *J. Am. Chem. Soc.* **1989**, *111*, 6865.

(12) Erler, B. S.; Scholz, W. F.; Lee, Y. J.; Scheidt, W. R.; Reed, C. A. *J. Am. Chem. Soc.* **1987**, *109*, 2644.

(13) Whittaker, M. M.; Chuang, Y.-Y.; Whittaker, J. W. *J. Am. Chem. Soc.* **1993**, *115*, 10029.

(14) Ito, N.; Phillips, S. E. V.; Yadav, K. D. S.; Knowles, P. F. *J. Mol. Biol.* **1994**, *238*, 794.

(15) Benelli, C.; Dei, A.; Gatteschi, D.; Pardi, L. *Inorg. Chem.* **1990**, *29*, 3409.

$(\mathrm{Tp}^{\mathrm{Cum,Me}})_2\mathrm{Co}$, $\mathrm{Tp}^{\mathrm{Cum,Me}}\mathrm{Co}$(3,5-DBSQ), and the Potential for Valence Tautomerism in Co(II)−SQ Complexes. Complexes of cobalt containing semiquinonate and catecholate ligands exhibit valence tautomerism associated with the transfer of an electron between a metal-based orbital and a quinone ligand orbital under conditions of thermal equilibrium.[5a] The complexes of Co and Mn that show this effect all consist of two chelated quinone ligands with nitrogen-donor ligands occupying the remaining two coordination sites of an octahedron (eq 1).

$$\mathrm{Co^{III}(N\text{-}N)(SQ)(Cat)} \rightarrow \mathrm{Co^{II}(N\text{-}N)(SQ)_2} \tag{1}$$

It has been of interest to determine whether this effect may be observed for other quinone complexes of cobalt. Thermodynamic properties that define the thermal conditions for equilibria are mainly associated with the change in charge and spin state of the metal, from low-spin Co(III) to high-spin Co(II).[17] In principle, complexes of Co containing a single quinone ligand may exhibit tautomeric equilibria (eq 2).

$$[\mathrm{Co^{III}(L)(Cat)}]^+ \rightarrow [\mathrm{Co^{II}(L)(SQ)}]^+ \tag{2}$$

The challenge becomes a matter of finding coligands (L) that give the correct balance of metal and quinone valence orbital energies. Several examples of complexes with the $[\mathrm{Co^{III}(L)(Cat)}]^+$ charge distribution are known. Brown reported $[\mathrm{Co^{III}(en)_2}$(3,5-DBCat)$]^+$ and $[\mathrm{Co^{III}(trien)}$(3,5-DBCat)$]^+$ 20 years ago.[18] More recently, Dei has described $[\mathrm{Co^{III}(CTH)}$(3,5-DBCat)$]^+$ [19] and reports that have included structure determinations have appeared for $(\eta^5\text{-}\mathrm{C_5(Me)_5})\mathrm{Co^{III}(Cat)}$ and $[\mathrm{(triphos)Co^{III}}$(3,5-DBCat)$]^+$.[20,21] Complexes of this charge distribution are diamagnetic and the metal ions show short Co−O bond lengths to the catecholate ligands as would be expected for low-spin d^6 Co(III). None of the complexes of this series have been reported to show evidence of tautomeric equilibria in solution or in the solid state.

Studies on synthetic routes to $\mathrm{Tp}^{\mathrm{Cum,Me}}\mathrm{Co}$(3,5-DBSQ), as a pyrazolylborate analog of $(\eta^5\text{-}\mathrm{C_5(Me)_5})\mathrm{Co^{III}(Cat)}$ and $[\mathrm{(triphos)Co^{III}}$(3,5-DBCat)$]^+$, indicated that the addition of hydroxide base was unnecessary and that the precursor complex contained only $\mathrm{Tp}^{\mathrm{Cum,Me}}$ and Co. The combination of Co^{2+} and $\mathrm{K[Tp^{Cum,Me}]}$ was observed to give $(\mathrm{Tp}^{\mathrm{Cum,Me}})_2\mathrm{Co}$, a complex that seemed unlikely given the stereochemistry of the pyrazolylborate ligand. The results of structural characterization on this complex are shown in Figure 5. Crystallographically imposed 2-fold symmetry relates the two $\mathrm{Tp}^{\mathrm{Cum,Me}}$ ligands. *Trans* bond angles of 170° listed in Table 4 show that the coordination geometry is octahedral. Co−N bond lengths are typical of high-spin Co(II) with a slight axial compression for the *trans* Co−N3 lengths. Cumenyl substituents of the two ligands mesh to completely encapsulate the metal in a hydrocarbon matrix defined by ligand methyl and isopropyl substituents.

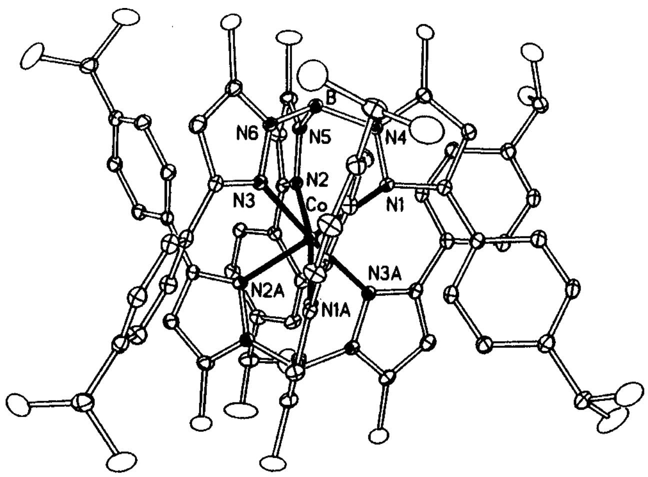

Figure 5. View of the $(\mathrm{Tp}^{\mathrm{Cum,Me}})_2\mathrm{Co}$ complex molecule.

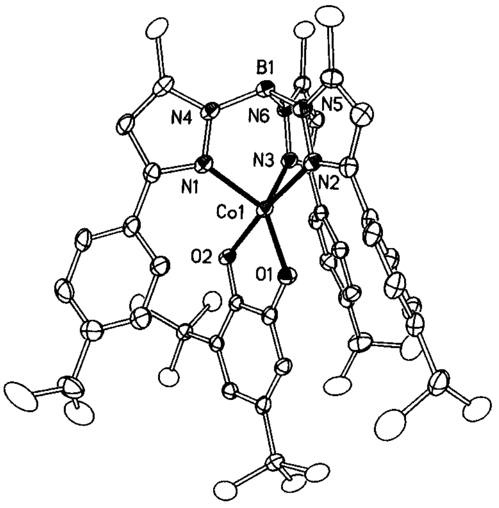

Figure 6. View of one of the independent $(\mathrm{Tp}^{\mathrm{Cum,Me}})\mathrm{Co}$(3,5-DBSQ) complex molecules.

Table 4. Selected Bond Lengths and Angles for $(\mathrm{Tp}^{\mathrm{Cum,Me}})_2\mathrm{Co}$

	Lengths (Å)		
Co−N1	2.257(2)	Co−N3	2.155(2)
Co−N2	2.219(2)		
	Angles (deg)		
N1−Co−N1′	99.26(8)	N1−Co−N3′	86.72(6)
N1−Co−N2	89.92(6)	N2−Co−N2′	81.08(8)
N1−Co−N3	86.53(6)	N2−Co−N3′	97.00(6)
N2−Co−N3	90.93(6)	N3−Co−N3′	169.58(8)
N1−Co−N2′	170.36(6)		

Despite the protective surface, $(\mathrm{Tp}^{\mathrm{Cum,Me}})_2\mathrm{Co}$ reacts with 3,5-DBCat in air to give $(\mathrm{Tp}^{\mathrm{Cum,Me}})\mathrm{Co}$(3,5-DBSQ). Crystallographic characterization on $(\mathrm{Tp}^{\mathrm{Cum,Me}})\mathrm{Co}$(3,5-DBSQ) (Figure 6) has indicated that it is isostructural with triclinic $(\mathrm{Tp}^{\mathrm{Cum,Me}})\mathrm{Zn}$(3,5-DBSQ). The coordination geometry is similar to the Zn complex as a distorted TBP. This appears clearly for the average O1−Co−N1 and O1−Co−N3 angles of 125.9(1) and 139.3(1)° listed in Table 3. $(\mathrm{Tp}^{\mathrm{Cum,Me}})\mathrm{Cu}$(3,5-DBSQ) is closer to SP and crystallizes in an unsolvated monoclinic unit cell. Bond lengths within the coordination sphere are typical of high-spin Co(II). Specifically, Co−O lengths are 0.1 Å longer than the Co(III) values of $(\eta^5\text{-}\mathrm{C_5(Me)_5})\mathrm{Co^{III}(Cat)}$ (1.837 Å) and $[\mathrm{(triphos)Co^{III}}$(3,5-DBCat)$]^+$ (1.864 Å). Accordingly, features of the 3,5-DBSQ ligand of $(\mathrm{Tp}^{\mathrm{Cum,Me}})\mathrm{Co}$(3,5-DBSQ) are typical of semiquinonates with C−O lengths that average 1.29 Å, and C−C bond lengths within the ring that reflect residual benzoquinone character.

Magnetic characterization on $(\mathrm{Tp}^{\mathrm{Cum,Me}})\mathrm{Co}$(3,5-DBSQ) is in accord with the $\mathrm{Co^{II}(SQ)}$ charge distribution. The plot of magnetic moment vs temperature given in Figure 4 shows that the complex has a magnetic moment of 4.0 μ_B at 350 K and

---

(16) Speier, G.; Csihony, J.; Whalen, A. M.; Pierpont, C. G. *Inorg. Chem.* **1996**, *35*, 3519.
(17) Pierpont, C. G.; Jung, O.-S. *Inorg. Chem.* **1995**, *34*, 4281.
(18) Wicklund, P. A.; Brown, D. G. *Inorg. Chem.* **1976**, *15*, 396.
(19) Benelli, C.; Dei, A.; Gatteschi, D.; Pardi, L. *Inorg. Chim. Acta* **1989**, *163*, 99.
(20) Bianchini, C.; Masi, D.; Mealli, C.; Meli, A.; Martini, G.; Laschi, F.; Zanello, P. *Inorg. Chem.* **1987**, *26*, 3683.
(21) Miller, E. J.; Rheingold, A. J.; Brill, T. B. *J. Organomet. Chem.* **1984**, *273*, 377.

that magnetic moment drops with decreasing temperature. Noninteracting $S = {}^{3}/_{2}$ and $S = {}^{1}/_{2}$ centers would combine to give a magnetic moment of 4.24 μ_B; the $S = 1$ spin state that would arise from strong antiferromagnetic exchange would have a magnetic moment of 2.83 μ_B. The experimental value at 350 K shows the effects of antiferromagnetic exchange, in contrast to the magnetic properties of (Tp$^{\mathrm{Cum,Me}}$)Cu(3,5-DBSQ), and the temperature dependence shown in Figure 4 results from a combination of magnetic and electronic effects of high-spin Co(II). Orbital contributions to the total moment may also be present. At temperatures below 10 K effective magnetic moment drops below the strongly coupled $S = 1$ value.

Electrochemical characterization on (Tp$^{\mathrm{Cum,Me}}$)Co(3,5-DBSQ) gives the same result that was observed for the Zn and Cu complexes (Table 2). Ligand-based Cat/SQ and irreversible SQ/BQ oxidations appear at −1.12 and +0.24 V, respectively (Figure 1), with no evidence for Co(II) oxidation within the potential range ±1.7 V. This result is in striking contrast to the electrochemistry on [Co$^{\mathrm{III}}$(CTH)(3,5-DBCat)]$^+$, which shows a reversible Co(II)/Co(III) couple at −0.69 V (vs SCE) on the negative side of the quinone ligand potentials and the Cat/SQ couple at +0.235 V.[19]

It is clear from the structural and magnetic properties of (Tp$^{\mathrm{Cum,Me}}$)Co(3,5-DBSQ) that the charge distribution is different from other isoelectronic cobalt complexes containing a single quinone ligand. It is particularly unusual that the pyrazolylborate ligand should result in the Co(II) charge distribution, while phosphine and Cp* coligands result in Co(III). This result implies that nitrogen atoms of the the Tp$^{\mathrm{Cum,Me}}$ ligand are surprisingly weak-field donors. Reasons for this property appear to be steric rather than electronic. The bulky cumenyl groups, coupled with the volume occupied by the 3,5-DBSQ ligand, restrict the extent to which the nitrogen donors can approach the central metal. This is a tentative explanation for an unanticipated result, but it is significant in demonstrating that coligand effects can be used to direct charge distribution in cobalt complexes containing one quinone ligand. Valence tautomerism may be observed with the appropriate coligand, and the bulky pyrazolylborate ligands may be the correct choice.

Acknowledgment. Support for this research came from the National Science Foundation and the Cristol Fund. M.R. thanks the Deutsche Forschungsgemeinschaft for a Postdoctoral Research Fellowship. We thank the NIST Laboratory, Boulder, CO, for use of their SQUID magnetometer.

Supporting Information Available: Tables of crystal data and intensity collection parameters, fractional coordinates, atomic displacement parameters, and fixed hydrogen coordinates for (Tp$^{\mathrm{Cum,Me}}$)Zn(3,5-DBSQ), (Tp$^{\mathrm{Cum,Me}}$)Cu(3,5-DBSQ), (Tp$^{\mathrm{Cum,Me}}$)Co(3,5-DBSQ), and (Tp$^{\mathrm{Cum,Me}}$)$_2$Co (64 pages). Crystallographic files, in CIF format, are available. Ordering and/or access information is given on any current masthead page.

IC970244T