Synthesis and Structure of an Air-Stable, Free-Radical Cobalt(III) Semiquinone Complex

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The air-stable, free-radical, low-spin Co(III) complex, $(Bu_4N)_2$ [3,5-Co(DBSQ)(CN)$_4$]·$^1/_2$H$_2$O·$^1/_4$CH$_2$Cl$_2$ (**1**), where 3,5-DBSQ is the semiquinone anion derived from the one-electron reduction of 3,5-di-*tert*-butyl-1,2-benzoquinone, has been synthesized by the reaction of the cobalt(II) tetramer [Co(3,5-DBSQ)$_2$]$_4$ with Bu$_4$NCN in THF. This is a cyanide-induced redox reaction resulting in the formation of cobalt (II) and cobalt(III) products as follows, where 3,5-DBCat is the respective catecholate dianion: [Co(3,5-DBSQ)$_2$]$_4$ + 8CN$^-$ → 2[Co(3,5-DBSQ)(CN)$_4$]$^{2-}$ + 2[Co(3,5-DBSQ)$_2$(3,5-DBCat)]$^{2-}$. The Co(III) product, $(Bu_4N)_2$ [Co(3,5-DBSQ)(CN)$_4$], is insoluble in THF while the Co(II) product remains in solution. Single-crystal X-ray diffraction of (**1**) reveals octahedrally coordinated cobalt(III) and C−O and C−C bond lengths indicative of semiquinone. The cyanide ligands occupy the remaining four sites with essentially linear Co−CN bond angles and average Co−C and Co−O bond distances of 1.89(2) Å and 1.97(2) Å, respectively. The complex has a magnetic moment of 1.80 μ_B and a typical semiquinone, S = $^1/_2$, free-radical EPR signature (CH$_2$Cl$_2$ solution, 293K) with g = 2.002, a_{Co} = 8.8G, and a_H = 2.6G. The identity of [Co(3,5-DBSQ)$_2$(3,5-DBCat)]$^{2-}$ (**2**) in the above reaction was confirmed by independent in situ generation of this anion from the reaction of [Co(3,5-DBSQ)$_2$]$_4$ with 3,5-DBCat^{2-} solution.

Introduction

Since the mid 1970s there has been a profusion of studies concerning the coordination chemistry of orthoquinones.[1] This surge of interest has been due, in part, to the richness of this chemistry, its relevance to biological electron-transfer processes involving catecholates, and also, perhaps, to the fascinating unpredictability often encountered in this chemistry.

Our interest in metalloquinone chemistry concerns the reactions of the Lewis base cyanide with metalloquinone oligomers and the subsequent formation of mixed-donor monomeric species containing coordinated, free-radical semiquinone and cyanide. It is related to and builds upon the earlier work of Pierpont, Hendrickson, and co-workers,[2−7] in which they study the reactivity of the tetramer [Co(3,5-DBSQ)$_2$]$_4$[8] with bidentate nitrogen donor ligands such as 2,2′-bipyridine and the properties of the adducts which are formed. The reaction with these bidentate ligands is rather straightforward: oligomer dissociation is followed by cis coordination of the bidentate ligand and formation of six-coordinate monomeric product as might be expected. The remarkable feature, however, is the valence tautomerism, as shown below for the 2,2′-bipyridine adduct. This involves a low-spin Co(III) ground state with both catecholate and semiquinone, and a thermally accessible, high-spin Co(II) excited state.[2]

$$Co(3,5\text{-}DBSQ)(3,5\text{-}DBCat)(bipy) \rightleftharpoons Co(3,5\text{-}DBSQ)_2(bipy) \quad (1)$$
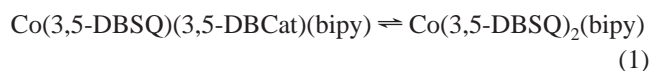
In this work, we examine the parallel reaction of [Co(3,5-DBSQ)$_2$]$_4$ with cyanide ion. Our intent was to prepare the previously unreported dicyano adduct [Co(3,5-DBSQ)$_2$(CN)$_2$]$^{2-}$ and investigate the possibilities for valence tautomerism and geometrical isomerism, but surprisingly the tetracyanocobalt(III) species [Co(3,5-DBSQ)(CN)$_4$]$^{2-}$ formed instead. The synthesis, properties, and single-crystal X-ray structure of (Bu$_4$N)$_2$[Co-(3,5-DBSQ)(CN)$_4$]·$^1/_2$H$_2$O·$^1/_4$CH$_2$Cl$_2$ (**1**) are reported along with a rationale for the apparent nonexistence of [Co(3,5-DBSQ)$_2$-(CN)$_2$]$^{2-}$.

Experimental Section

Materials. All reactions were carried out under argon using standard Schlenk techniques. Reagent-grade THF was distilled under nitrogen from sodium benzophenone. 3,5-Di-*tert*-butyl-1,2-benzoquinone was purchased from Lancaster Synthesis. 3,5-Di-*tert*-butylcatechol, tetrabutylammonium cyanide, and 1.0 M tetrabutylammonium hydroxide in methanol were purchased from Aldrich Chemical. [Co(3,5-DBSQ)$_2$]$_4$ was prepared by the procedure of Pierpont et al.,[9] with toluene substituted for benzene as solvent. All other chemicals were reagent-grade and commercially available.

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(5) Adams, D. M.; Hendrickson, D. N. *J. Am. Chem. Soc.* **1996**, *118*, 11515.

(6) Roux, C.; Adams, D. M.; Itié, J. P.; Polian, A.; Hendrickson, D. N.; Verdaguer, M. *Inorg. Chem.* **1996**, *35*, 2846.

(7) Adams, D. M.; Noodleman, L.; Hendrickson, D. N. *Inorg. Chem.* **1997**, *36*, 3966.

(8) Abbreviations: 3,5-DBQ = 3,5-di-*tert*-butyl-1,2-benzoquinone; 3,5-DBSQ = 3,5-di-*tert*-butyl-1,2-benzosemiquinone; 3,5-DBCatH$_2$ = 3,5-di-*tert*-butyl-*o*-catechol

(9) Buchanan, R. M.; Fitzgerald, B. J.; Pierpont, C. G. *Inorg. Chem.* **1979**, *18*, 3439.

Table 1. Selected Crystallographic Data for **1**

formula	$C_{50.25}H_{93.5}CoCl_{0.5}N_6O_{2.5}$
fw	898.50
space group	$P2_1/c$
a, Å	27.5207(3)
b, Å	18.4345(3)
c, Å	22.1614(3)
β, deg	102.4330(10)
V, Å^3	10 979.5(3)
Z	8
T, °C	-111
λ, Å	0.710 73
crystal size, mm	$0.72 \times 0.42 \times 0.08$
ρ_{calc}, g cm^{-3}	1.098
μ, cm^{-1}	3.79
absorption correction	SADABS
transmission factors	$0.71-0.97$
no. of unique data	15 764
no. data with $I/\sigma(I) > 2$, N_o	8668
no. parameters, N_p	1115
R ($wR2$), %[a]	9.80(24.91)

[a] Refinement method is full-matrix least-squares on F^2; weighted R-factors $wR2$ are based on F^2 for all data, conventional R-factor R is based on F; $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$, $wR2 = [\Sigma w(F_o{}^2 - F_c{}^2)^2/\Sigma w(F_o{}^2)^2]^{1/2}$, $w^{-1} = \sigma^2(F_o{}^2) + (0.1653P)^2$, $P = (F_o{}^2 + 2F_c{}^2)/3$.

Synthesis of (Bu$_4$N)$_2$[Co(3,5-DBSQ)(CN)$_4$]·^{1}/$_2$H$_2$O·^{1}/$_4$CH$_2$Cl$_2$ (1). To a solution of [Co(3,5-DBSQ)$_2$]$_4$ (0.600 g; 0.300 mmol) in 25 mL of THF, solid Bu$_4$NCN (0.645 g, 2.40 mmol) was added with stirring. The immediately resulting purple solution was stirred for 18 h. The air-stable, purple microcrystalline solid that formed was filtered, washed with 5 mL of ice-cold THF, and dried under vacuum. Recrystallization was effected by slow diffusion of diethyl ether into a solution of the above solid dissolved in CH$_2$Cl$_2$. Yield: 0.39 g (37%). Anal. Calcd for $C_{50.25}H_{93.5}CoCl_{0.5}N_6O_{2.5}$: C, 67.15; H, 10.49; N, 9.36. Found: C, 67.34; H, 10.17; N, 9.27. IR (KBr, cm^{-1}): ν_{CN} 2133 (sh), 2124 (sh), 2120 (s); ν_{CO} 1485 (s),1456 (s); ν_{CoC} 417 (m); ν_{OH} 3446 (s); δ_{HOH} 1635 (m).
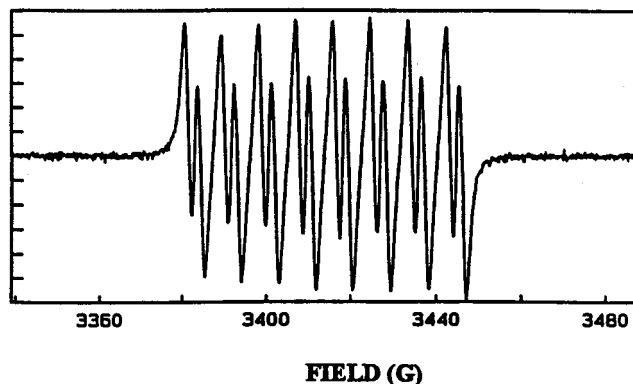
In Situ Preparation of [Co(3,5-DBSQ)$_2$(3,5-DBCat)]$^{2-}$ (2). A solution of 1.0 M Bu$_4$NOH in methanol (1.0 mL, 1.0 mmol), was added, via syringe and with stirring, to a solution of 3,5-DBCatH$_2$ (0.111 g, 0.499 mmol) in 15 mL THF. The resulting solution was transferred by cannula, with stirring, to a solution of [Co(3,5-DBSQ)$_2$]$_4$ (0.254 g, 0.127 mmol) in 15 mL of THF and stirred for 18 h, resulting in a burgundy-colored solution.

Instrumentation. Infrared spectra were recorded from 4000 to 400 cm^{-1} with a Mattson Galaxy 5000 FTIR spectrometer. Electronic spectra were obtained from 220 to 2500 nm using an HP 8452 diode array spectrometer and an Olis-modified Cary 14 spectrophotometer. Magnetic susceptibility was measured with a Johnson Matthey Magnetic Susceptibility balance. The EPR spectrum was obtained with a Bruker ECS spectrometer at 9.5 GHz at the University of British Columbia. Elemental analyses were performed by Quantitative Technologies, Inc.

X-ray Diffraction Study of 1. Many crystals (>20, all obtained by recrystallization as described above) were examined on the diffractometer. The crystals occurred as very thin plates, which generally yielded poor diffraction patterns that often could not be satisfactorily indexed. Four data sets were collected, only one of which refined satisfactorily (although all data sets gave the structure described herein). Selected details of the X-ray diffraction experiment are given in Table 1.

Diffraction data were obtained by using a Bruker SMART-CCD X-ray system. Data were processed by using Bruker SMART system software and the Bruker SAINT program for integration of data frames.[10a] The data were corrected for absorption by means of the program SADABS.[10c] All subsequent computations were performed by using the SHELXTL program suite.[10b] The structure was solved by

(10) (a) Bruker AXS, Inc.; (b) Sheldrick, G. M., SHELXTL, version 5, Bruker Analytical X-ray Division, Madison, WI, 1994. (c) Sheldrick, G. M., SADABS, a program for Bruker area detector absorption correction (to be published).

Figure 1. EPR spectrum of **1** in CH$_2$Cl$_2$ at room temperature.

direct methods and refined by full-matrix least-squares methods. Hydrogen atoms were included in the structural model at calculated positions.

Near the end of refinement, a site partially occupied by a molecule of the recrystallization solvent, methylene chloride, was identified. Further refinement (with constraints applied to the C–Cl bond lengths) led to a site-occupancy factor of 50% for the atoms of this methylene chloride, although the displacement parameters for the atoms of this occluded solvent molecule remained large. At that point, additional electron density well above background level was still present in the electron-density map (major peak 2.6 e Å^{-3}). Given that the analysis and the IR spectrum both suggested the presence of water in the crystals, two of the largest electron-density peaks were modeled as partial oxygen atoms, despite their chemically surprising locations. Site-occupancy factors for these two oxygen atoms refined to approximately 40 and 30%. While this falls short of the 50% H$_2$O (see formulation above) indicated by microanalysis, remaining electron-density peaks were below 1 e Å^{-3} (with the exception of a peak of approximately 1.4 e Å^{-3} only 0.7 Å from Co) and were judged not worth pursuing. Large displacement parameters ($U_{eq} > 0.1$ Å^2) for some of the atoms of complex A (C18A–C20A) and its counterions (C37A, C46A, C50A, C58A) were consistent with their positions as terminal carbon atoms of t- or n-butyl groups; reasonable attempts to describe these atoms using disordered models did not give satisfactory refinement.

Results and Discussion

The preparation of mixed-ligand, cobalt–quinone–cyanide complexes has been undertaken from two pathways: reaction of cyanide with a cobalt(II) semiquinone tetramer (the approach taken in this work) and reaction of pentacyanocobaltate(II) ion with orthoquinone as reported previously by Vlček, et al.[11] In the latter investigation, the reaction was monitored by EPR, and no attempt was made to isolate product.

Reaction of CN$^-$ and [Co(3,5-DBSQ)$_2$]$_4$ in an 8:1 molar ratio in THF produces **1** in approximately 35–45% yield rather than the anticipated (Bu$_4$N)$_2$[Co(3,5-DBSQ)$_2$(CN)$_2$]. This complex is completely air-stable as a solid and in solution. From the EPR spectrum of **1** in CH$_2$Cl$_2$ solution (Figure 1), it is evident that coordinated semiquinone free radical ($S = {}^1/_2$) is present. The observed eight-line spectrum ($g = 2.002$) is due to coupling with ^{59}Co ($I = {}^7/_2$) with further splitting being due to the 4-H ring proton. The respective coupling constants are $a_{Co} = 8.8$ G and $a_H = 2.6$ G. These hyperfine coupling constants are consistent with those from previously reported examples of semiquinone bound to cobalt (III),[2,12] including that of the

(11) Vlček, A., Jr.; Klíma, J.; Vlček, A. A. *Inorg. Chim. Acta* **1983**, *69*, 191.

(12) (a) Wicklund, P. A.; Beckmann, L. S.; Brown, D. G. *Inorg. Chem.* **1976**, *15*, 1996. (b) Simándi, L. I.; Barna, T.; Argay, G.; Simándi, T. L. *Inorg. Chem.* **1995**, *34*, 6337.
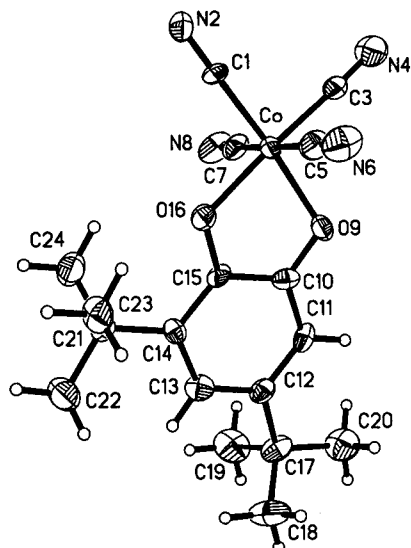
Figure 2. Thermal ellipsoid plot (50% probability level) showing the molecular structure and numbering scheme of the [Co(3,5-DBSQ)-(CN)$_4$]$^{2-}$ anion in **1**.

[Co(3,5-DBSQ)(CN)$_4$]$^{2-}$ ion that was generated in the reaction of Co(CN)$_5$$^{3-}$ with 3,5-DBQ in dimethylformamide solution,[11] and indicate that the unpaired electron is localized principally on the semiquinone. Consistent with the presence of free-radical, $S = \frac{1}{2}$, semiquinone bound to diamagnetic, d^6 Co(III), the measured magnetic susceptibility of **1** at 295 K is 1.80 μ_B.

The results of the single-crystal X-ray structural analysis of **1**, while limited in their precision, are sufficient to identify the product unambiguously as the tetracyano complex. In crystals of **1**, the asymmetric unit contains two formula units. The structure and numbering scheme for [Co(3,5-DBSQ)(CN)$_4$]$^{2-}$ is shown in Figure 2. Selected atomic coordinates are listed in Table 2 and bond distances and angles are listed in Table 3. The coordination geometry of [Co(3,5-DBSQ)(CN)$_4$]$^{2-}$ is cis-octahedral with an O–Co–O bite angle of 82.4(2)° (83.8(2)° for complex A). The range of C–O bond lengths for structurally characterized first-row transition-metal quinone complexes is quite narrow: 1.29(1) Å and 1.35(1) Å, respectively, for coordinated semiquinonate(1−) and catecholate(2−).[3] With an average C–O distance of 1.29(2) Å, the quinone ligand in **1** has the definite metric characteristics of a semiquinone. Also the two short, four long, intraring C–C distance pattern observed in **1** is similarly characteristic of semiquinone with its localized C–C double-bond character. The C–N bond distances range from 1.141(9) to 1.171(8) Å, and the Co–C–N bond angles are all essentially linear. Both parameters are as expected for coordinated cyanide ion. The four Co–C bond lengths form two distinct groups: those trans to cyanide (av 1.910(8) Å) and those trans to semiquinone (av 1.874(8) Å). The Co–O bond lengths average 1.97(2) Å, somewhat long for low-spin cobalt(III), whereas the comparable distances range from 1.851 to 1.906 Å in the low-spin Co(III) complex [Co(3,5-DBSQ)-(3,5-DBCat)(bipy)].[2] The strong affinity of cyanide for cobalt(III) most likely is the cause for the lengthening of the trans Co–O bonds in **1**.

The presence of the residual electron density treated as fractional oxygen atoms (see above) in the final model is puzzling, especially given their location; one peak is sandwiched between cyano carbon atoms C1 and C3 (C···O 1.8−1.9 Å), while the other is only 1.64 Å from C5A. Frankly, we would have been tempted to attribute this electron density to an

Table 2. Selected Atomic Coordinates and Equivalent Isotropic Displacement Coefficients (Å^2) for **1**^{a}

	x	y	z	U(eq)^a
Co	0.1267(1)	0.7275(1)	−0.2738(1)	0.022(1)
C1	0.1239(3)	0.8049(4)	−0.3293(3)	0.028(2)
N2	0.1225(2)	0.8512(4)	−0.3639(3)	0.034(2)
C3	0.1880(3)	0.6986(4)	−0.2898(4)	0.031(2)
N4	0.2249(3)	0.6803(4)	−0.3019(4)	0.054(2)
C5	0.1604(3)	0.7882(4)	−0.2081(4)	0.034(2)
N6	0.1801(3)	0.8257(4)	−0.1687(3)	0.048(2)
C7	0.0968(3)	0.6636(4)	−0.3400(4)	0.033(2)
N8	0.0781(3)	0.6250(4)	−0.3798(3)	0.047(2)
O9	0.1246(2)	0.6446(3)	−0.2161(2)	0.027(1)
C10	0.0810(3)	0.6356(4)	−0.2076(4)	0.026(2)
C11	0.0655(3)	0.5739(4)	−0.1781(3)	0.027(2)
C12	0.0170(3)	0.5670(4)	−0.1712(3)	0.027(2)
C13	−0.0172(3)	0.6247(4)	−0.1927(4)	0.029(2)
C14	−0.0059(2)	0.6864(4)	−0.2233(3)	0.023(2)
C15	0.0442(3)	0.6925(4)	−0.2304(3)	0.024(2)
O16	0.0608(2)	0.7469(2)	−0.2577(2)	0.030(1)
C17	−0.0031(3)	0.4989(4)	−0.1459(4)	0.034(2)
C18	−0.0273(4)	0.5167(5)	−0.0927(4)	0.055(3)
C19	−0.0409(4)	0.4643(5)	−0.1980(4)	0.053(2)
C20	0.0383(3)	0.4428(4)	−0.1236(4)	0.051(3)
C21	−0.0450(3)	0.7430(4)	−0.2498(4)	0.033(2)
C22	−0.0965(3)	0.7254(5)	−0.2376(4)	0.048(2)
C23	−0.0290(3)	0.8188(4)	−0.2198(4)	0.041(2)
C24	−0.0484(3)	0.7473(4)	−0.3198(4)	0.044(2)
CoA	0.3529(1)	0.2500(1)	0.3222(1)	0.013(1)
C1A	0.2873(3)	0.2400(4)	0.2773(3)	0.022(2)
N2A	0.2477(2)	0.2327(3)	0.2489(3)	0.036(2)
C3A	0.3297(2)	0.3108(4)	0.3776(3)	0.016(2)
N4A	0.3149(2)	0.3478(3)	0.4121(3)	0.031(2)
C5A	0.3605(2)	0.3323(4)	0.2731(3)	0.017(2)
N6A	0.3659(2)	0.3825(3)	0.2441(3)	0.029(2)
C7A	0.3452(2)	0.1695(4)	0.3733(3)	0.018(2)
N8A	0.3416(2)	0.1195(3)	0.4047(3)	0.031(2)
O9A	0.3788(2)	0.1841(2)	0.2673(2)	0.017(1)
C10A	0.4262(2)	0.1743(3)	0.2864(3)	0.015(2)
C11A	0.4541(3)	0.1249(3)	0.2584(3)	0.024(2)
C12A	0.5045(3)	0.1171(4)	0.2794(3)	0.024(2)
C13A	0.5285(3)	0.1632(4)	0.3292(3)	0.027(2)
C14A	0.5039(2)	0.2122(4)	0.3594(3)	0.022(2)
C15A	0.4510(2)	0.2165(3)	0.3388(3)	0.017(2)
O16A	0.4228(2)	0.2575(2)	0.3647(2)	0.017(1)
C17A	0.5340(3)	0.0597(4)	0.2530(4)	0.033(2)
C18A	0.5279(6)	−0.0122(6)	0.2845(7)	0.148(8)
C19A	0.5177(4)	0.0486(8)	0.1887(6)	0.135(7)
C20A	0.5904(4)	0.0704(7)	0.2724(7)	0.109(5)
C21A	0.5322(3)	0.2598(4)	0.4131(4)	0.036(2)
C22A	0.5141(3)	0.2401(4)	0.4723(4)	0.044(2)
C23A	0.5204(3)	0.3403(4)	0.3956(4)	0.046(2)
C24A	0.5883(3)	0.2500(5)	0.4250(5)	0.068(3)

^{a} U(eq) is defined as one-third of the trace of the orthogonalized **U**$_{ij}$ tensor.
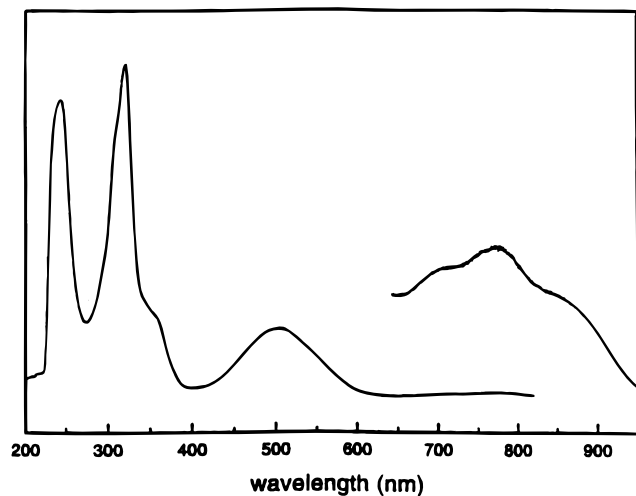
anomaly in the data if it were not for the microanalysis (which fit well with $\frac{1}{2}$ molecule of water per formula unit), the IR spectrum of recrystallized sample (which contained vibrational bands associated with water), and the reasonableness of the remainder of the structure. Given the great difficulty that we had in finding a crystal that was suitable for X-ray diffraction study (see above), collection of yet another data set was judged to be impractical.

Consistent with the above structure, the infrared spectrum of **1** shows C–N stretching vibrations at 2120, 2124, and 2133 cm^{-1}, while the characteristic semiquinone C–O stretching vibrations occur at 1485 and 1456 cm^{-1} and the Co–C stretching vibration at 417 cm^{-1}. At 0.4-cm^{-1} resolution, only three of the four symmetry-allowed ν_{CN} bands predicted for the cis configuration of [Co(3,5-DBSQ)(CN)$_4$]$^{2-}$ are clearly discernible. Since very small ν_{CN} band separations are not

Table 3. Selected Interatomic Distances (Å) and Angles (deg) for the Two Anions in the Asymmetric Unit of **1**[a]

Co–C1	1.874(8)	1.874(7)
Co–C3	1.875(8)	1.873(7)
Co–C5	1.909(8)	1.903(7)
Co–C7	1.923(9)	1.906(7)
Co–O16	1.954(5)	1.956(4)
Co–O9	2.001(5)	1.958(4)
O9–C10	1.264(8)	1.295(7)
C10–C11	1.423(10)	1.418(9)
C10–C15	1.470(10)	1.440(9)
C11–C12	1.382(10)	1.372(9)
C12–C13	1.434(10)	1.436(10)
C13–C14	1.392(10)	1.385(9)
C14–C15	1.426(9)	1.432(9)
C15–O16	1.303(8)	1.302(7)
C1–Co–C3	90.2(3)	89.0(3)
C1–Co–C5	89.9(3)	89.6(3)
C3–Co–C5	90.0(4)	89.2(3)
C1–Co–C7	90.9(3)	88.8(3)
C3–Co–C7	86.4(3)	91.2(3)
C5–Co–C7	176.3(3)	178.3(3)
C1–Co–O16	94.2(3)	94.6(2)
C3–Co–O16	174.0(3)	176.4(3)
C5–Co–O16	94.1(3)	90.1(2)
C7–Co–O16	89.4(3)	89.6(2)
C1–Co–O9	176.1(3)	177.5(2)
C3–Co–O9	93.1(3)	92.7(2)
C5–Co–O9	92.1(3)	92.3(2)
C7–Co–O9	87.3(3)	89.3(2)
O16–Co–O9	82.4(2)	83.8(2)

[a] Parameters for anion A (drawing not shown) are listed in column 2.

Figure 3. UV–vis absorption spectrum of **1** in CH$_2$Cl$_2$ at room temperature.

uncommon for metallocyanides,[13] the remaining unobserved band must be part of the 2120-cm^{-1} band envelope.

The UV–vis spectrum of **1** in CH$_2$Cl$_2$ is shown in Figure 3; the band maxima are listed in Table 4. Two distinct sets of bands are seen in the spectrum of **1**. The first set is in the 200–600 nm region. These bands have molar absorptivities (ϵ) greater than 2,000 and are probably metal–to–ligand charge-transfer transitions involving both cyanide and semiquinone. The second set is a band envelope 10-fold less intense centered at approximately 800 nm. Comparable low-intensity bands either do not exist or were not detected in the absorption spectra of two related Co(III) semiquinone complexes, Co(salen)(3,5-
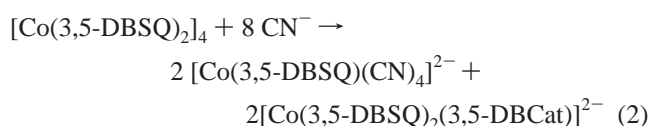
Table 4. Electronic Spectral Data

cmpnd	λ_{max}, nm (ϵ)
1[a]	244 (8,400), 322 (9,200), 356 (2,400), 504 (2,100) 701 (310), 774 (360), 846 (260)
2[b]	528 (1.0), 742 (1.0), 874 (1.5)

[a] Recorded in dichloromethane. [b] Recorded in THF; ϵ values reflect relative intensities.

DBSQ)[14,15] and [Co(trien)(3,5-DBSQ)]$^{2+}$.[12a,16] However, similar low-intensity bands were found centered at 950 nm in the spectrum of [Cr(tren)(3,6-DBSQ)]$^{2+}$ and were attributed to $n \rightarrow \pi^*$ semiquinone transitions.[17,18] More directly, a similar low-intensity band envelope centered at 700 nm was reported by Pierpont and co-workers for the solution spectrum of free-radical 3,6-DBSQ in the salt [Co(C$_5$H$_5$)$_2$][3,6-DBSQ].[19]

The reaction between cyanide and [Co(3,5-DBSQ)$_2$]$_4$ is a redox reaction in which cobalt(II) is oxidized to cobalt(III). With 50% of the cobalt unaccounted for in this reaction, it seemed plausible to look for evidence of a cobalt(II) catecholate complex remaining in the filtrate, assuming that the oxidizing agent is semiquinone which is then converted to catecholate.
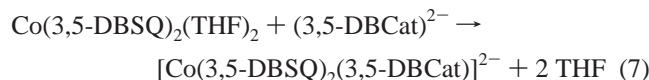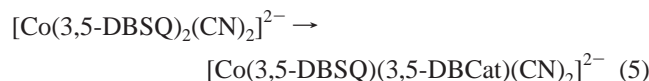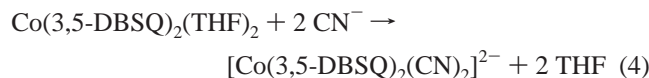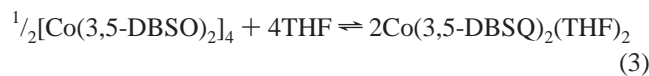
The visible spectrum band maxima and relative intensities of the filtrate are listed in Table 4. Because the bands at 536, 742, and 874 nm are of comparable intensity, it is highly unlikely that the latter two are $n \rightarrow \pi^*$ semiquinone transitions. Most likely, all three are metal–to–ligand charge-transfer bands. The above three-band pattern is suggestive of a cobalt(II) semiquinone species. Absorption bands of similar energy are found in the spectrum of [Co(3,5-DBSQ)$_2$]$_4$ and all of the [Co(3,5-DBSQ)$_2$(N–N)] diiminium adducts and were suggested to be characteristic of cobalt(II) semiquinone complexes.[2,3] We believe that the principal absorbing species in solution is [Co(3,5-DBSQ)$_2$(3,5-DBCat)]$^{2-}$ (which may, itself, be valence-tautomeric) and that it is formed by the redox reaction shown below.

$$[Co(3,5\text{-}DBSQ)_2]_4 + 8\,CN^- \rightarrow$$
$$2\,[Co(3,5\text{-}DBSQ)(CN)_4]^{2-} +$$
$$2[Co(3,5\text{-}DBSQ)_2(3,5\text{-}DBCat)]^{2-} \quad (2)$$

This could occur in a rapid, stepwise fashion, beginning with dissociation of the tetramer and followed, sequentially, by coordination of cyanide to Co(II), internal electron transfer from Co(II) to DBSQ, and further substitution of cyanide to produce [Co(3,5-DBSQ)(CN)$_4$]$^{2-}$ and [Co(3,5-DBSQ)$_2$(3,5-DBCat)]$^{2-}$. This is conceptualized in the following scheme.[20,21]

(13) See, for example, the ν_{CN} frequencies for K[Co(en)(CN)$_4$]: Ripan, R.; Fårcas, A.; Piringer, O. *Z. Anorg. Allg. Chem.* **1966**, *346*, 211.

(14) Kessel, S. L.; Emberson, R. M.; Debrunner, P. G.; Hendrickson, D. N. *Inorg. Chem.* **1980**, *19*, 1170.

(15) Salen is the dianion of the tetradentate ligand *N,N'*-ethylenebis-(salicylidenimine).

(16) Trien is the tetradentate ligand triethylenetetramine.

(17) Wheeler, D. E.; McCusker, J. K. *Inorg. Chem.* **1998**, *37*, 2296.

(18) Tren is the tetradentate ligand tris(2-aminoethyl)amine.

(19) Lange, C. W.; Conklin, B. J.; Pierpont, C. G. *Inorg. Chem.* **1994**, *33*, 1276.

(20) Tetrameric [Co(3,5-DBSQ)$_2$]$_4$ contains both terminal and bridging oxygen donor atoms, the latter atoms bridging between two and three cobalt atoms. It would not be unreasonable to expected modest oligomer dissociation in solution, probably at a bridging oxygen. This would create vacant sites for facile coordination of cyanide.

(21) Although eq 6 implies rapid ligand substitution at a Co(III) center, precedent exists when a strong trans-labilizing group such as cyanide is coordinated. Wilkins, R. G. *Kinetics and Mechanism of Reactions of Transition Metal Complexes*, 2nd ed.; VCH: Weinheim, Germany, 1991; Chapter 8.

$$^1/_2[\text{Co}(3,5\text{-DBSO})_2]_4 + 4\text{THF} \rightleftharpoons 2\text{Co}(3,5\text{-DBSQ})_2(\text{THF})_2 \quad (3)$$

$$\text{Co}(3,5\text{-DBSQ})_2(\text{THF})_2 + 2\ \text{CN}^- \rightarrow$$
$$[\text{Co}(3,5\text{-DBSQ})_2(\text{CN})_2]^{2-} + 2\ \text{THF} \quad (4)$$

$$[\text{Co}(3,5\text{-DBSQ})_2(\text{CN})_2]^{2-} \rightarrow$$
$$[\text{Co}(3,5\text{-DBSQ})(3,5\text{-DBCat})(\text{CN})_2]^{2-} \quad (5)$$

$$[\text{Co}(3,5\text{-DBSQ})(3,5\text{-DBCat})(\text{CN})_2]^{2-} + 2\ \text{CN}^- \rightarrow$$
$$[\text{Co}(3,5\text{-DBSQ})(\text{CN})_4]^{2-} + (3,5\text{-DBCat})^{2-} \quad (6)$$

$$\text{Co}(3,5\text{-DBSQ})_2(\text{THF})_2 + (3,5\text{-DBCat})^{2-} \rightarrow$$
$$[\text{Co}(3,5\text{-DBSQ})_2(3,5\text{-DBCat})]^{2-} + 2\ \text{THF} \quad (7)$$

To test this hypothesis and confirm with reasonable likelihood that the filtrate from the THF synthesis of **1** contains [Co(3,5-DBSQ)$_2$(3,5-DBCat)]$^{2-}$, we have prepared this anion by an independent route. A solution of 3,5-DBCatH$_2$ dissolved in THF was deprotonated with Bu$_4$NOH to generate 3,5-DBCat^{2-}. The solution of catecholate dianion was then added to [Co(3,5-DBSQ)$_2$]$_4$ tetramer in a 4:1 molar ratio, with the expectation that tetramer dissociation followed by catecholate coordination would produce **2**. The resulting burgundy solution with its electronic spectrum identical to that of the filtrate from **1** provides reasonable supporting evidence for the reaction stoichiometry shown in eq 2. Unfortunately, the extreme air sensitivity of this solution has thwarted our attempts to isolate crystals of (Bu$_4$N)$_2$[Co(3,5-DBSQ)$_2$(3,5-DBCat)].

Why is [Co(3,5-DBSQ)$_2$(CN)$_2$]$^{2-}$ or its valence tautomer not formed in the 2:1 mole-ratio reaction of cyanide with Co(3,5-DBSQ)$_2$? The great affinity of Co(III) for cyanide and other strong-field ligands is well-known as is the thermodynamic stability of Co(III) cyanide complexes.[22] Were cyanide and 2,2′-bipyridine[2] similar in ligand-substitution reactivity with [Co(3,5-DBSQ)$_2$]$_4$, the Co (III) complex [Co(3,5-DBSQ)(3,5-DBCat)-(CN)$_2$]$^{2-}$ would be expected as the sole tautomeric product. Apparently it is the great affinity of Co(III) for cyanide (four being preferable to two) and the preference of Co(II) over Co(III) for oxygen donor ligands, which provides the thermodynamic driving force for the reaction scheme as proposed above.

Supporting Information Available: Listings of crystal and structure refinement data, atomic coordinates, bond lengths and angles, anisotropic displacement parameters, and hydrogen coordinates. This material is available free of charge via the Internet at http://pubs.acs.org.

IC981052G

(22) Greenwood, N. N.; Earnshaw, A. *Chemistry of the Elements*; Pergamon Press: Oxford, 1984; Chapter 26.