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Low-Energy Catechol to Cobalt(III) Electron Transfer in the Cobaloxime-Catalyzed Oxidation of 3,5-Di-*tert*-butylcatechol

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Intermediates of the catalytic oxidation of 3,5-di-*tert*-butylcatechol (3,5-DTBCatH_2) by O_2 in the presence of (triphenylphosphine)bis(dimethylglyoximato)cobalt(II) as catalyst have been studied. The complex [Co(Hdmg)$_2$-(Ph$_3$P)(3,5-DTBCatH)] has been isolated from the reaction mixture and characterized by X-ray diffraction (monoclinic, $P2_1/c$, a = 16.498(1) Å, b = 9.254(1) Å, c = 26.038(2) Å, β = 103.59(1)°, V = 3864.0(4) Å^3, D_c = 1.33 g cm^{-3}, Z = 4, μ(Cu Kα) = 44.4 cm^{-1}, R = 0.0480). It contains a unidentate 3,5-di-*tert*-butylcatecholato-(1−) ligand. Upon dissolution and warming in benzene under N_2, homolytic Co−O bond cleavage produces cobaloxime(II) and the free 3,5-di-*tert*-butylsemiquinonato(1−) anion radical, as demonstrated by ESR spectroscopy. In O_2-containing solution, the complex restarts the catalytic reaction, during which the [Co^{III}(Hdmg)$_2$(Ph$_3$P)(3,5-DTBSQ$^\bullet$)] species can also be detected by ESR. The observed behavior is rationalized by a mechanism incorporating the intermediates identified.

There has been considerable recent interest in bistable cobalt(III) complexes containing 3,5-di-*tert*-butylcatecholato(2−) (3,5-DBCat) and 3,5-di-*tert*-butylsemiquinonato(1−) (3,5-DBSQ) ligands with 2,2′-bipyridine and 9,10-phenanthroline type diimine coligands.[1,2] This behavior may be of potential use in sensors and switches in molecular electronic devices.[3] In toluene solution, a temperature-dependent redox equilibrium between Co(III) and Co(II) valence tautomers has been demonstrated by magnetic and spectroscopic measurements.[1a] In solid samples, transition temperatures for this reaction, involving electron transfer from the 3,5-DBCat ligand to Co^{III} and subsequent Co^{II} spin crossover, are in the range 180−320 K, depending on the coligand.[1b]

The catalytic oxidation of 3,5-DBCatH_2 by O_2 in the presence of copper and iron complexes has been studied with the objective of modeling catechol dioxygenase action, which involves ring cleavage and oxygen incorporation. This type of oxidation occurs via intermediates in which the catechol is chelated to the metal ion and dioxygen attacks the diol moiety.[4a]

In the course of our studies on the catalytic oxidation of 3,5-DBCatH_2 in the presence of Co(Hdmg)$_2$(Ph$_3$P)$_2$, where Hdmg is dimethylglyoximato(1−), we have isolated and characterized a new cobaloxime(III) derivative, [Co(Hdmg)$_2$(Ph$_3$P)(3,5-DBCatH)] (**2**), containing the unidentate 3,5-DBCatH$^-$ ligand in the axial position. Upon dissolution in benzene under N_2 at room temperature, it exhibits a strong band at 630 nm (ϵ = 7700 M^{-1} cm^{-1}), indicating electron transfer (eq 1) between closely lying ligand and metal orbitals. Similar behavior has been observed in various semiquinonato complexes and can be regarded as due to an intramolecular redox equilibrium.[1c]

$$[\mathrm{Co^{III}(Hdmg)_2(Ph_3P)(3,5{-}DBCatH)}] \rightleftharpoons [\mathrm{Co^{II}(Hdmg)_2(Ph_3P)(3,5{-}DBSQH^\bullet)}] \quad (1)$$

Upon warming of the solution to 330 K, the free anion radical 3,5-DBSQ$^{\bullet-}$ and cobaloxime(II) can be detected by their ESR signals, corresponding to homolytic Co−O bond dissociation according to eq 2. This reaction demonstrates that catechol to

$$[\mathrm{Co^{III}(Hdmg)_2(Ph_3P)(3,5{-}DBCatH)}] \rightleftharpoons [\mathrm{Co^{II}(Hdmg)_2(Ph_3P)}] + 3,5{-}\mathrm{DBSQ}^{\bullet-} + \mathrm{H}^+ \quad (2)$$

cobalt(III) electron transfer of the type shown in eq 1 may be thermally enhanced to the point of homolytic Co−O bond cleavage when the catechol is bonded via only one of its two donor O atoms and suitable coligands are present. We now describe experiments that show how reaction 2 is related to the catalytic oxidation of 3,5-DBCatH_2 by the cobaloxime(II)/O_2 system, modeling the catecholase activity of tyrosinase.[5]

The reaction of dioxygen with a solution of [Co^{II}(Hdmg)$_2$-(Ph$_3$P)$_2$] (1.626 g, 2 mmol) and 3,5-DBCatH_2 (0.444 g, 2 mmol) in 50 mL of acetone was followed by gas volumetry at room temperature. After 50% catechol conversion to 3,5-di-*tert*-butyl-

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Table 1. Crystallographic Data for the Complex [Co(Hdmg)$_2$(Ph$_3$P)(3,5-DBCatH)] (**2**)

chem formula	CoPC$_{40}$N$_4$O$_6$H$_{49}$	fw	771.77
a, Å	16.498(1)	space group	$P2_1/c$
b, Å	9.254(1)	*T*, °C	21
c, Å	26.038(2)	λ, Å	1.541 84
α, deg	90.00	ρ_{calcd}, g cm^{-3}	1.33
β, deg	103.59(1)	μ, cm^{-1}	44.4
γ, deg	90.00	$R(F_o)^a$	0.048
V, Å^3	3864.0(4)	$R_w(F_o)^b$	0.054
Z	4		

^{a} $R = \sum||F_o| - |F_c||/\sum|F_o|$. ^{b} $R_w = \{\sum w(|F_o| - |F_c|^2/\sum w|F_o|^2\}^{1/2}$.

1,2-benzoquinone (3,5-DBQ), evaporation to one-third volume afforded dark blue crystals of **2** (yield 58%), which were characterized by X-ray crystallography and elemental analysis (Table 1).[6]

The molecular structure of **2** is given in Figure 1. The geometry around the central cobalt atom is octahedral, in line with earlier structural information on bis(dimethylglyoximato)cobalt complexes.[7] A remarkable feature is that the 3,5-di-*tert*-butylcatecholato(1−) ligand occupies an axial position of the square-planar cobaloxime, being bound in a unidentate fashion via the oxygen atom in position 1 of the 3,5-DTBC ring. This structure is a result of the very stable square-planar geometry and the steric constraint of the bulky *tert*-butyl groups, determining the choice of bonding O atom. The uncoordinated hydroxy group is not involved in either intra- or intermolecular hydrogen bonding. The most informative crystallographic data for the characterization of catechol complexes are the C−O and the C1−C2 bond lengths, as they are sensitive to the ligand charge and bonding. The C−O bond lengths for chelated catecholato ligands are reasonably constant around 1.35 Å, while those for semiquinone ligands lie close to 1.28 Å.[1e] The C1−O11 distance of 1.341(5) Å in **2** is consistent with unidentate catecholato coordination and a protonated O21 [C2−O21 = 1.386(5) Å]. The C1−C2 distance of 1.403(5) Å is quite close to the 1.39 Å observed in catecholates as opposed to the 1.44 Å in semiquinones.[1e] These bond distances are in good agreement with the corresponding data reported for unidentate Fe-bonded catecholato,[5c] Ti-bonded 3,5-di-*tert*-butylcatecholato,[5d] and Fe-bonded tetrachlorocatecholato[1g] ligands.

The four equatorial N donor atoms are coplanar within ±0.048(3) Å with the cobalt atom displaced by 0.078(1) Å above their mean plane toward the PPh$_3$ molecule. The planes of the two Hdmg$^-$ ligands make an angle of 14.7°. The planarity of the Co(Hdmg)$_2$ units is in good agreement with the relevant data observed for organocobaloximes.[7] Both the 3,5-DTBC and PPh$_3$ ligands are nearly perpendicular to the equatorial plane. The mean Co−N bond length is 1.886 Å. The Co(Hdmg)$_2$(3,5-DTBC)(PPh$_3$) fragment is characterized by an O−Co−P angle of 176.7(2)° and Co−O and Co−P bond lengths of 1.969(3) and 2.316(1) Å, respectively.

Table 2. Fractional Atomic Coordinates and B_{eq} Values for Non-Hydrogen Atoms in **2** with Their Estimated Standard Deviations in Parentheses

atom	*x*	*y*	*z*	B_{eq}, Å^2,^{a}
Co1	0.78626(4)	0.38838(8)	0.04585(3)	2.43(1)
P2	0.76240(7)	0.3684(1)	0.12972(5)	2.69(3)
C11	0.7620(3)	0.5409(5)	0.1630(2)	3.1(1)
C12	0.8376(3)	0.6130(6)	0.1772(2)	4.3(1)
C13	0.8458(3)	0.7427(6)	0.2031(2)	4.9(1)
C14	0.7787(3)	0.8057(6)	0.2163(2)	5.5(2)
C15	0.7039(3)	0.7346(6)	0.2045(3)	6.5(2)
C16	0.6950(3)	0.6041(6)	0.1776(2)	5.1(1)
C21	0.8325(3)	0.2681(5)	0.1827(2)	2.8(1)
C22	0.8152(3)	0.2700(6)	0.2325(2)	4.0(1)
C23	0.8625(3)	0.1940(6)	0.2746(2)	4.5(1)
C24	0.9283(3)	0.1147(6)	0.2673(2)	4.6(1)
C25	0.9479(3)	0.1125(7)	0.2194(2)	4.8(1)
C26	0.8996(3)	0.1879(6)	0.1768(2)	3.9(1)
C31	0.6631(3)	0.2781(5)	0.1267(2)	3.0(1)
C32	0.6621(3)	0.1318(6)	0.1373(2)	4.1(1)
C33	0.5872(3)	0.0587(6)	0.1323(2)	5.2(1)
C34	0.5134(3)	0.1293(7)	0.1168(2)	5.7(2)
C35	0.5122(3)	0.2727(7)	0.1044(2)	5.1(2)
C36	0.5868(3)	0.3485(6)	0.1084(2)	4.0(1)
O11	0.8008(2)	0.4125(3)	−0.0266(1)	3.4(8)
N7A	0.7613(2)	0.1917(4)	0.0360(1)	2.68(8)
O1A	0.6316(2)	0.5327(3)	0.0098(1)	3.92(8)
N2A	0.6707(2)	0.4056(4)	0.0172(1)	2.79(8)
C3A	0.6312(3)	0.2861(5)	0.0007(2)	3.0(1)
C4A	0.5422(3)	0.2790(7)	−0.0282(2)	4.7(1)
C5A	0.6847(3)	0.1581(5)	0.0129(2)	3.0(1)
C6A	0.6556(3)	0.0078(6)	0.0002(2)	5.0(1)
O8A	0.8191(2)	0.0866(3)	0.0498(1)	3.61(8)
O1B	0.9439(2)	0.2483(3)	0.0650(1)	3.45(8)
N2B	0.9045(2)	0.3741(4)	0.0657(1)	2.72(8)
C3B	0.9454(3)	0.4942(5)	0.0715(2)	2.9(1)
C4B	1.0371(3)	0.5026(6)	0.0794(2)	4.9(1)
C5B	0.8912(3)	0.6219(5)	0.0655(2)	3.3(1)
C6B	0.9231(4)	0.7721(6)	0.0732(2)	5.4(2)
N7B	0.8128(2)	0.5875(4)	0.0536(1)	3.04(9)
O8B	0.7540(2)	0.6922(4)	0.0456(1)	4.40(9)
O21	0.6717(2)	0.4973(4)	−0.1008(1)	4.82(9)
C1	0.7729(3)	0.3191(5)	−0.0661(2)	2.7(1)
C2	0.7050(2)	0.3624(5)	−0.1065(2)	2.6(1)
C3	0.6731(3)	0.2762(5)	−0.1501(2)	2.8(1)
C4	0.7102(3)	0.1415(5)	−0.1513(2)	3.3(1)
C5	0.7779(3)	0.0929(5)	−0.1119(2)	3.2(1)
C6	0.8089(3)	0.1854(6)	−0.0705(2)	3.2(1)
C41	0.6022(3)	0.3290(6)	−0.1953(2)	3.5(1)
C42	0.6294(3)	0.4644(6)	−0.2204(2)	5.0(2)
C43	0.5765(3)	0.2129(7)	−0.2394(2)	5.5(2)
C44	0.5240(3)	0.3604(7)	−0.1756(2)	5.7(2)
C51	0.8154(3)	−0.0571(6)	−0.1159(2)	4.4(1)
C52	0.8638(6)	−0.1078(9)	−0.0619(3)	16.1(3)
C53	0.8753(5)	−0.0533(8)	−0.1498(3)	10.4(2)
C54	0.7518(5)	−0.1659(8)	−0.1341(6)	18.1(5)

^{a} Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $B_{eq} = (8\pi^2/3)[a^2B_{11} + b^2B_{22} + c^2B_{33} + ab(\cos\gamma)B_{12} + ac(\cos\beta)B_{13} + bc(\cos\alpha)B_{23}]$. The anisotropic temperature factor expression is $\exp[-2\pi^2(B_{11}a^{*2}h^2 + ... + 2B_{12}a^*b^*hk + ...)]$.

The catalytic oxidation of 3,5-DBCatH$_2$ was also monitored by ESR spectroscopy at room temperature (10^{-2} M catalyst and substrate were dissolved in benzene in an ESR tube under air, and the tube was placed into the cavity within about 1 min). The spectrum observed (Figure 2) is the superposition of two spectra. Spectrum a exhibits all the features characteristic for Co(III) complexes of the 3,5-DBSQ$^{\bullet-}$ anion radical[1f,2c-f] and

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(6) X-ray diffraction data were collected on an Enraf-Nonius CAD4 X-ray diffractometer, using graphite-monochromated Cu Kα radiation. $F(000) = 1628$; $N_{tot} = 7889$; $-20 \le h \le 20$; $0 \le k \le 11$; $0 \le l \le 32$; 3552 reflections with $I > 3\sigma(I)$ and $2.8 < \theta < 74.3°$ (crystal size 0.05 × 0.08 × 0.30 mm; needle). The structure was solved by direct methods, using the program SHELXS and subsequent structure factor and Fourier calculations.[8] Refinement was done by full-matrix techniques. No absorption correction was made. The H atom positions were generated from assumed geometries and were taken into account without refinement in structure factor calculations with isotropic temperature factors taken from the *International Tables for Crystallography* (1962). Program system used: MolEN (1990) on a VAX 3100 computer.[9] Anal. Found: C, 62.3; N, 7.2; P, 4.0; H, 6.5. Calcd: 61.2; N, 7.2; P, 3.9; H, 6.7.

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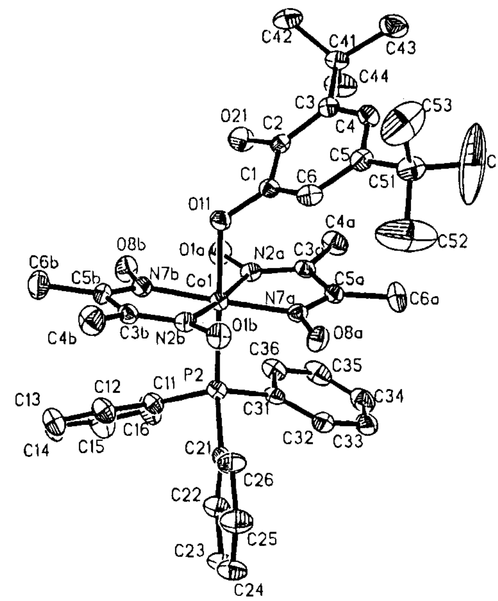


Figure 1. Molecular structure of [Co(Hdmg)$_2$(Ph$_3$P)(3,5-DBCatH)] (**2**). Selected bond lengths (Å): Co1−O11 = 1.969(3); Co1−N7A = 1.870(4); Co1−N2A = 1.884(3); Co1−N2B = 1.902(2); Co1−N7B = 1.893(4); Co−P2 = 2.316(1); C1−O11 = 1.341(5); C2−O21 = 1.386(5); C1−C2 = 1.403(5); C1−C6 = 1.389(7); C2−C3 = 1.386(6); C3−C4 = 1.393(6); C4−C5 = 1.401(6); C5−C6 = 1.379(6); O1A−N2A = 1.333(5). Selected bond angles (deg): O11−Co1-N7A = 92.9(2); O11−Co1−N2A = 87.2(2); P2−Co1−O11 = 176.7(2); P2−Co1−N2A = 90.0(2); P2−Co1−N7A = 88.4(2); N7A−Co1−N2A = 81.8(2); N7B−Co1−N2B = 80.9(2); O11−C1−C2 = 117.5(6); O11−C1−C6 = 124.1(6); O21−C2−C1 = 116.3(6); O21−C2−C3 = 121.5(5).

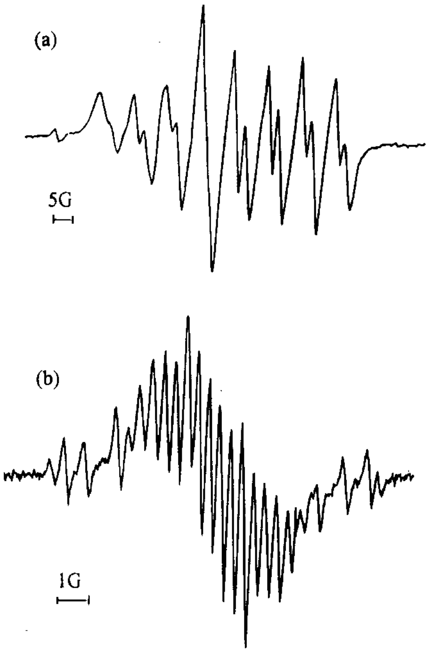
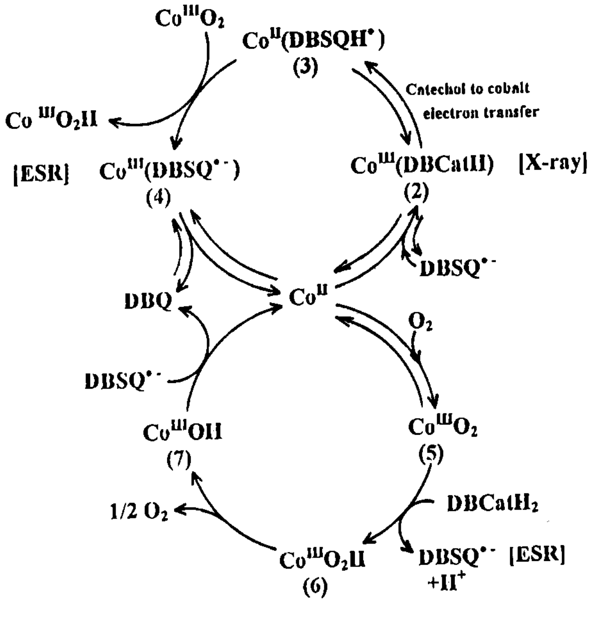


Figure 2. ESR spectra of free radical intermediates observed during the cobaloxime(II)-catalyzed oxidation of 3,5-DTBCatH_2 in benzene at room temperature: (a) eight-line pattern due to Co^{III}(3,5-DBSQ$^•$) (**4**) with an unresolved singlet at the center due to free 3,5-DBSQ$^{•-}$; (b) resolved spectrum of the central singlet.

Scheme 1



can be attributed to Co^{III}(Hdmg)$_2$(3,5-DBSQ) (**4**). Its eight-line pattern is centered at $g = 2.0017$ due to ^{59}Co coupling and shows a hyperfine coupling constant of 10.4 G. Each line is split into a doublet due to the C4 proton (3.3 G) of the semiquinone ligand. The second component of the spectrum ($g = 2.0046$), observable at higher resolution (b), can be assigned as the (solvent-separated) ion pair [Ph$_3$PH$^+$][3,5-DBSQ$^{•-}$], in which the cation is bonded to the C1−O$^-$ anion and the unpaired electron is localized mainly on C2−O$^•$ (phenoxyl type radical). This structure would make the two *m*-protons and the two *t*-Bu groups equivalent and would not require coupling with the phosphorus atom. The coupling constants of a_{2H} = 1.7 G and a_{18H} = 0.35 G simulate the observed spectra very well. In contrast, assignments as 3,5-DBSQH$^•$ or the free 3,5-DBSQ$^{•-}$ anion radical do not give satisfactory simulated spectra with the parameters reported for these or similar structures[10 a,c].

Similar to the reactions of [Co(CN)$_5$]$^{3-}$ [10b,c] and Co^{II}(saphen)[10d] with quinones, the formation of **4** via oxidative addition from DBQ and Co^{II} can also be observed by ESR spectroscopy under Ar atmosphere (benzene, RT, 10^{-2} M reactants), but no free DBSQ$^{•-}$ is detectable under these conditions. Under O$_2$ this reaction is suppressed due to the high rate of Co^{II} oxygenation to Co^{III}O$_2$ and the high reactivity of the superoxo complex.[4b]

The observed behavior and the intermediates detected are consistent with the mechanism of catechol oxidation depicted in Scheme 1, where Co^{II} stands for [Co^{II}(Hdmg)$_2$(Ph$_3$P)]. The second Ph$_3$P is lost upon dissolution of the starting [Co^{II}(Hdmg)$_2$(Ph$_3$P)$_2$].[11]

According to this scheme, the catalytic activation of dioxygen is due to the formation of the known superoxocobaloxime **5**, which, via H atom abstraction, generates the DBSQ$^{•-}$ anion radical, detected by ESR spectroscopy (lower cycle). The latter combines with paramagnetic cobaloxime(II) to afford the isolated **2**, whose redox isomer **3** is further oxidized to the other ESR-active species **4**, having a ligand-centered unpaired electron (upper cycle). The latter may also form via oxidative addition of the product DBQ to Co^{II} . Intermediates **5**−**7** are required by the lack of H$_2$O$_2$ formation, *i.e.* reduction of O$_2$ to water. In the related oxidative dehydrogenation of 2-aminophenol,[12] the transformation of **6** to **7** was invoked to explain the rapid initial

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O_2-uptake of 0.5 mol of O_2/mol of cobaloxime and the absence of (μ-peroxo)dicobaloxime during this period. The catalyst Co^{II} is regenerated via reduction of $Co^{III}OH$ by $DBSQ^{\bullet-}$. The intermediates in Scheme 1 have either been identified in this work or are known from earlier studies on cobaloxime chemistry.[4b] Involvement of the analogues of **5**–**7** has been widely demonstrated in catalytic oxidations with cobalt Schiff-base complexes.[4a]

Scheme 1 represents a functional model of the catecholase activity of tyrosinase based on free radical type intermediates in which the key role is played by ligand to metal electron transfer.

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Supporting Information Available: Tables giving structure determination details, complete positional and isotropic thermal parameters, and anisotropic thermal parameters of the non-H atoms and a unit cell packing diagram for **2** (9 pages).

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