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Cobalt Superoxo and Alkylperoxo Complexes Derived from Reaction of Ring-Cleaving Dioxygenase Models with O₂

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Abstract

The syntheses and O₂ reactivities of active-site models of cobalt-substituted ring-cleaving dioxygenases are presented. The pentacoordinate cobalt(II)-aminophenolate complex, [Co(Tp^{Me2}) (tBu²APH)], gives rise to two distinct dioxygen adducts at reduced temperatures. The first is a paramagnetic (*S* = 1/2) cobalt(III)-superoxo species that was characterized with spectroscopic and computational techniques. The identity of the second Co/O₂ adduct was elucidated by X-ray crystallography, which revealed an unprecedented cobalt(III)-alkylperoxo structure generated by O₂ addition to the metal ion and ligand. These results provide synthetic precedents for proposed intermediates in the catalytic cycles of O₂-activating cobalt enzymes.

The bacterial breakdown of organic compounds, including human-generated pollutants, often requires dioxygenase enzymes that oxidatively cleave aromatic carbon–carbon bonds using O₂.¹ Substrates of these ring-cleaving dioxygenases include substituted catechols, *o*-aminophenols, 1,4-hydro-quinones, and salicylates.² The active sites of most ring-cleaving dioxygenases feature a mononuclear nonheme iron center bound facially to one Glu (or Asp) and two His residues.³ However, recent studies revealed that an extradiol catechol dioxygenase (CatD), homoprotocatechuate-2,3-dioxygenase (HPCD), exhibits equal or greater activity with Mn or Co in the active site.⁴ The “promiscuity” of HPCD supports the mechanistic proposal that O₂ activation by ring-cleaving dioxygenases does not necessitate a change in metal oxidation state. Instead, the metal facilitates the transfer of one electron from the coordinated substrate to O₂, thereby yielding a M(II)-superoxo species with an (imino)semiquinone radical (**B** in Scheme 1).⁵ Formation of a substrate-based radical encourages attack by the superoxide ligand to generate a putative alkylperoxo species (**C**), which undergoes rearrangement to insert an O atom into the substrate ring (**D**).⁶ Analogous mechanisms are likely employed by *o*-aminophenol and 1,4-hydroquinone dioxygenases.⁷

The surprising activity of metal-substituted HPCD has stimulated the synthesis of extradiol CatD models featuring Co and Mn. Yet complexes that replicate the monoanionic, bidentate

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Supporting Information

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Experimental procedures, computational methods and models, spectroscopic data (EPR, ¹H NMR, UV-vis) (PDF)

Crystallographic information (CIF)

coordination of the catecholate ligand in the enzyme active site are still lacking. Recently, the Riordan and Hikichi groups reported Co and Mn complexes, respectively, that feature a monoanionic catecholate ligand bound in a monodentate manner.^{8,9} Exposure of these complexes to O₂ results in formation of the corresponding M(II)-semiquinonate (SQ) species via loss of an electron and proton (i.e., net H atom transfer, HAT). Thus, the CatD models fail to replicate the initial O₂ binding step of the enzymatic mechanism. In some cases, further reaction of the Co(II)-SQ complexes with O₂ affords the intradiol ring-cleavage products in low yield.⁸

To avoid the shortcomings of the cobalt-catecholate complexes, we decided to pursue cobalt(II) dioxygenase models that contain an aminophenolate ligand instead. Aminophenol dioxygenases (APDOs) are closely related to extradiol CatDs both structurally and mechanistically,² and although a cobalt-substituted APDO has not been generated to date, it is reasonable to expect such an enzyme to display activity. More importantly, we reckoned that the less acidic –NH₂ donor would deter formation of a Co(II)-iminosemiquinone (ISQ) species and provide access to biologically relevant O₂ reaction pathways. This hypothesis proved correct, and herein we describe the synthesis of two mononuclear Co(II) complexes (**1** and **2** in Figure 1) that feature a monoanionic, bidentate aminophenolate ligand. The 2-histidine-1-carboxylate facial triad of the enzymatic active site is modeled with the Tp^{R2} ligand (R = Ph (**1**) or Me (**2**); Tp^{R2} = hydrotris(pyrazolyl-1-yl)borate substituted with R-groups at the 3- and 5-positions). Although HAT reactivity is observed for **1** and **2** under certain conditions, the latter complex gives rise to O₂-derived intermediates not observed for the analogous catecholate complexes, including a cobalt-superoxo species that resembles intermediate **B**. Furthermore, we report the first X-ray structure of a cobalt-alkylperoxo complex with a structure akin to **C** in the proposed ring-cleaving mechanism.

The crystal structures of complexes **1** and **2** each revealed a five-coordinate Co(II) center in which the monoanionic ^tBu²APH ligand binds in a bidentate fashion (Figure 1). The Tp^{R2} ligands coordinate facially with average Co–N_{Tp} bond distances of 2.11 Å. The Co–N/O bond distances (Table S1) are characteristic of pentacoordinate, high-spin Co(II) complexes. X-band EPR spectra of **1** and **2** (Figure S3) exhibit features arising from the m_s = ±3/2 doublet of the S = 3/2 manifold (D < 0). In both spectra, hyperfine splitting from the ⁵⁹Co nucleus is evident in the low-field resonance near g ~ 7 (A_{Co} = 85 G for **2**).

Complex **1** reacts slowly with O₂ to yield a stable, dark green species (**1**^{ox}; Figure 2a). X-ray crystallography determined that **1**^{ox}, like its precursor, is a neutral five-coordinate complex. The Co–N_{Tp} bond distances change only slightly from **1** to **1**^{ox} (Table S1), suggesting that the Co center remains divalent and high-spin. Despite these similarities, comparison of the two structures reveals that the ^tBu²APH ligand of **1** has been oxidized to an ISQ radical in **1**^{ox}. The change is apparent in the shorter O1–C1 and N2–C2 bond distances of **1**^{ox}, as well as the quinoidal distortion of its C–C bonds (Figure 2b). Using the “metrical oxidation state” method developed by Brown,¹⁰ the ^tBu²ISQ ligand of **1**^{ox} carries a charge of –0.95, near the ideal value of –1.0 for an ISQ ligand. The presence of an ^tBu²ISQ radical is also evident from characteristic π → π* features in the 600–800 nm region of the absorption spectrum that overlap with Co(II) d-d bands (Figure 2a).¹¹ Complex **1**^{ox} is EPR-silent and the

observed magnetic moment of $2.9 \mu_B$ ($S = 1$) is indicative of antiferromagnetic coupling between the Co(II) and $^{tBu_2}ISQ$ spins.

Likewise, exposure of **2** to O_2 at room temperature (RT) yields a green species (2^{ox}) with spectral and magnetic properties similar to 1^{ox} (Figure S4). A notable difference, however, is that 2^{ox} decays within minutes at 20 °C, which hindered the growth of suitable crystals. Significantly, 2^{ox} can also be generated under anaerobic conditions by treating **2** with one equivalent of 2,4,6-tri-*tert*-butylphenoxy radical (TTBP $^{\bullet}$), a well-known H atom abstractor (Figure S4). This result demonstrates that the conversion of **2** $\rightarrow$ 2^{ox} involves loss of a proton and electron to generate $[Co^{II}(Tp^{Me_2})-(^{tBu_2}ISQ)]$. Nuclear magnetic resonance (NMR) analysis of the reaction mixture after decay of 2^{ox} in air found that 3,5-di-*tert*-butyl- α -benzoquinone (DTBQ) is the only product derived from the $^{tBu_2}APH$ ligand (Figure S5). Thus, the overall O_2 reaction does not result in oxygenated or ring-cleaved products; instead, the $^{tBu_2}APH$ ligand undergoes two-electron oxidation to the corresponding α -iminobenzoquinone, followed by hydrolysis to DTBQ upon aqueous workup.

While the O_2 reactivity of **1** and **2** at RT is dominated by HAT chemistry, we found that it is possible to observe novel Co/ O_2 adducts at reduced temperatures. Reaction of **2** with O_2 at -78 °C in CH_2Cl_2 or THF generates a metastable pink species (**2- O_2**) with absorption features at $\lambda_{max} = 505$ and 800 nm (Figure 3a). Purging the solution with Ar does not regenerate **2**, and warming causes **2- O_2** to convert to 2^{ox} . The X-band EPR spectrum of **2- O_2** presents a $S = 1/2$ signal with g -values of 2.084, 2.007, 1.957 and ^{59}Co hyperfine splitting of 28 G (Figure 3b). Quantification of the EPR signal indicates that **2- O_2** accounts for ~80% of the Co in the sample, with the remainder being starting complex. Both the UV-vis and EPR spectra of **2- O_2** are strikingly similar to those previously reported for Co/ O_2 adducts.¹² In particular, the clustering of the g -values near 2.0 and the small A_{Co} -value of **2- O_2** (relative to its Co(II) precursor) are distinctive characteristics of cobalt(III)-superoxo species, reflecting localization of the unpaired electron on the superoxo ligand. The presence of a superoxo-to-Co(III) charge transfer (CT) transition near 500 nm, as observed for **2- O_2** , is also a common feature of known cobalt(III)-superoxo complexes in noncorrinoid environments.¹² Interestingly, complex **1** is unreactive with O_2 at low temperatures, suggesting that sterics modulate the energetics of O_2 binding.

The geometric and electronic structures of **2- O_2** were further analyzed using density functional theory (DFT) calculations. The geometry-optimized structure (Figure S6) features an end-on superoxo ligand in a bent conformation. The superoxo nature of the O_2 ligand is reflected in the computed O–O distance of 1.278 Å. The six-coordinate Co(III) center is low-spin and nearly all of the unpaired spin density resides on the superoxo ligand, consistent with the EPR data. The computed ^{59}Co **A**-tensor is anisotropic with a dominant hyperfine splitting of 26 G, in excellent agreement with the experimental value. The g -values predicted by CASSCF/NEVPT2 calculations ($g_{1,2,3} = 2.060, 1.991$ and 1.979) reproduce the weak anisotropy of the **2- O_2** signal. Thus, the computational data further corroborate the assignment of **2- O_2** as a cobalt(III)-superoxo species.

Interestingly, we found that a second Co/ O_2 adduct with spectroscopic features distinct from **2- O_2** is generated when 2^{ox} is treated with O_2 at reduced temperatures. Aerobic solutions of

2^{ox} in CH₃CN and CH₂Cl₂ change from dark green to light brown upon cooling. Monitoring the process by UV–vis spectroscopy revealed that the species generated at low temperature (**3**) lacks well-defined absorption features in the visible region (Figure 4a). The absorption features of **2^{ox}** return when the solution is warmed to RT, but full intensity is not recovered due to its instability. No color change is observed during cooling if **2^{ox}** is generated anaerobically via reaction with TTBP[•], indicating that formation of **3** requires O₂. The characteristics of the **2^{ox}** → **3** conversion are reminiscent of those previously reported for the O₂ reaction of cobalt(II)-semiquinonate complexes at reduced temperatures.^{8b,9b} Because of this, we prepared and structurally characterized [Co^{II}(Tp^{Me2})(^tBu²SQ)] (**4**; Figure S7), the SQ analogue of **2^{ox}**. Complex **4** reacts with O₂ at *T* < −40 °C to give a brown chromophore (**5**) with absorption features similar to those of **3** (Figure S8). Like **3**, species **5** is EPR-silent and variable-temperature NMR experiments indicate that both Co/O₂ adducts are diamagnetic (Figures S9–S11).

Due to its stability at temperatures below −25 °C, we succeeded in growing light brown crystals of **3** for X-ray analysis. The resulting crystal structure revealed a neutral cobalt-alkylperoxo complex in which the O₂-derived atoms form a bridge between Co and C1 of the ligand (Figure 4b), thereby generating a five-membered metallocycle. The O2–O3 distance of 1.482(3) Å is typical of alkylperoxo ligands, and the *sp*³ hybridization of the C1-atom is evident from its average bond angle of 110° ± 7°. The Co–N/O bond distances in **3** are shorter than those of **2** by an average of 0.15 Å, indicating a change from high-spin Co(II) to low-spin Co(III). Comparison of **3** to **1^{ox}** reveals that the quinoidal distortion of the ligand is far more pronounced in the former complex, and the metric parameters observed for **3** are characteristic of iminobenzoquinone ligands.¹⁰ Thus, formation of **3** is a two-electron process involving oxidation of both the Co center and ^tBu²ISQ ligand (Scheme 2).

The “spiroendoperoxide” structure of **3** is the first of its kind among first-row transition metal complexes; indeed, it represents the only X-ray structure to date of a synthetic dioxygen adduct with direct relevance to ring-cleaving dioxygenases. The closest analogues are Rh(III)- and Ir(III)-alkylperoxo complexes generated by O₂ addition to a 9,10-phenanthrene-catecholate(2-) ligand.¹³ Similarly, Gade recently reported a square-planar nickel(II) complex that features an alkylperoxometallocycle derived from O₂.¹⁴ In main-group chemistry, Abakumov showed that a series of Sb(V)-amidophenolate complexes reversibly bind O₂ to yield an alkylperoxo donor.¹⁵ As for biological precedents, the structure **3** closely resembles the iron-alkylperoxo intermediate observed by Lipscomb in a crystal structure of HPCD.¹⁶

As summarized in Scheme 2, we have explored the O₂ reaction landscape of two cobalt(II)-aminophenolate complexes. These studies led to the isolation and characterization of cobalt(III)-superoxo (**2-O₂**) and -alkylperoxo (**3**) species that mimic proposed intermediates of ring-cleaving dioxygenases. It is instructive that subtle differences between these synthetic Co/O₂ adducts and their enzymatic counterparts account for the lack of ring-cleavage activity exhibited by our synthetic models. Specifically, the low-spin Co(III) center of **3** stabilizes the alkylperoxo ligand and prevents subsequent O–O bond cleavage, whereas the high-spin Co(II) ion in the putative enzymatic intermediate facilitates insertion of the distal O atom into the ring via Criegee rearrangement. In our models, the inability of **2-O₂** to

convert to the requisite cobalt(II)-alkylperoxo intermediate is likely due to the lack of unpaired spin density within the $[\text{Co}^{3+}\text{-tBu}^2\text{APH}]$ unit, which hinders O–C bond formation. The enzyme avoids this scenario by coupling O_2 binding to a proton transfer from the substrate to a conserved second-sphere His residue. According to computational studies, this process yields a superoxo-Co(II)-substrate radical species (**B** in Scheme 1) that is primed for alkylperoxo formation.¹⁷ Future efforts in our laboratory will be directed toward the design of functional active-site mimics that replicate the ability of the enzyme to control both H^+ transfer and O_2 binding.

Supplementary Material

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REFERENCES

- (1). Wang Y; Li J; Liu A Oxygen activation by mononuclear nonheme iron dioxygenases involved in the degradation of aromatics. *JBIC, J. Biol. Inorg. Chem* 2017, 22, 395–405. [PubMed: 28084551]
- (2). Vaillancourt FH; Bolin JT; Eltis LD The ins and outs of ring-cleaving dioxygenases. *Crit. Rev. Biochem. Mol. Biol* 2006, 41, 241–267. [PubMed: 16849108]
- (3). (a)Koehntop KD; Emerson JP; Que L The 2-His-1-carboxylate facial triad: a versatile platform for dioxygen activation by mononuclear non-heme iron(II) enzymes. *JBIC, J. Biol. Inorg. Chem* 2005, 10, 87–93. [PubMed: 15739104] (b)Bruijninx PCA; van Koten G; Klein Gebbink RJM Mononuclear non-heme iron enzymes with the 2-His-1-carboxylate facial triad: recent developments in enzymology and modeling studies. *Chem. Soc. Rev* 2008, 37, 2716–2744. [PubMed: 19020684]
- (4). (a)Emerson JP; Kovaleva EG; Farquhar ER; Lipscomb JD; Que L Swapping metals in Fe- and Mn-dependent dioxygenases: Evidence for oxygen activation without a change in metal redox state. *Proc. Natl. Acad. Sci. U. S. A* 2008, 105, 7347–7352. [PubMed: 18492808] (b)Fielding AJ; Kovaleva EG; Farquhar ER; Lipscomb JD; Que L Jr. A hyperactive cobalt-substituted extradiol-cleaving catechol dioxygenase. *JBIC, J. Biol. Inorg. Chem* 2011, 16, 341–355. [PubMed: 21153851] (c)Fielding AJ; Lipscomb JD; Que L Jr. Characterization of an O_2 adduct of an active cobalt-substituted extradiol-cleaving catechol dioxygenase. *J. Am. Chem. Soc* 2012, 134, 796–799. [PubMed: 22175783] (d)Fiedler AT; Fischer AA Oxygen activation by mononuclear Mn, Co, and Ni centers in biology and synthetic complexes. *JBIC, J. Biol. Inorg. Chem* 2017, 22, 407–424. [PubMed: 27853875]
- (5). Fielding AJ; Lipscomb JD; Que L Jr. A two-electron-shell game: intermediates of the extradiol-cleaving catechol dioxygenases. *JBIC, J. Biol. Inorg. Chem* 2014, 19, 491–504. [PubMed: 24615282]
- (6). (a)Lipscomb JD Mechanism of extradiol aromatic ring-cleaving dioxygenases. *Curr. Opin. Struct. Biol* 2008, 18, 644–649. [PubMed: 19007887] (b)Kovaleva EG; Lipscomb JD Versatility of biological non-heme Fe(II) centers in oxygen activation reactions. *Nat. Chem. Biol* 2008, 4, 186–193. [PubMed: 18277980]
- (7). (a)Dong G; Lu J; Lai W Insights into the Mechanism of Aromatic Ring Cleavage of Noncatecholic Compound 2-Amino-phenol by Aminophenol Dioxygenase: A Quantum Mechanics/Molecular Mechanics Study. *ACS Catal.* 2016, 6, 3796–3803.(b)Machonkin TE; Doerner AE Substrate

Specificity of *Sphingobium chlorophenolicum* 2,6-Dichlorohydroquinone 1,2-Dioxygenase. *Biochemistry* 2011, 50, 8899–8913. [PubMed: 21870805]

- (8). (a)Wang P; Yap GPA; Riordan CG Five-coordinate MII-semiquinonate (M = Fe, Mn, Co) complexes: reactivity models of the catechol dioxygenases. *Chem. Commun* 2014, 50, 5871–5873.(b)Wang P; Yap GPA; Riordan CG Synthesis, characterization and O₂ reactivity of a bioinspired cobalt(II)-catecholate complex. *Inorg. Chim. Acta* 2019, 488, 49–55.
- (9). (a)Agake S.-i.; Komatsuzaki H; Satoh M; Agou T; Tanaka Y; Akita M; Nakazawa J; Hikichi S A monomeric manganese(II) catecholato complex: Synthesis, crystal structure, and reactivity toward molecular oxygen. *Inorg. Chim. Acta* 2019, 484, 424–429.(b)Ikeda A; Hoshino K; Komatsuzaki H; Satoh M; Nakazawa J; Hikichi S O₂ activation and external substrate oxidation capability of a Co(II)-semiquinonato complex. *New J. Chem* 2013, 37, 2377–2383.
- (10). Brown SN Metrical Oxidation States of 2-Amidophenoxide and Catecholate Ligands: Structural Signatures of Metal-Ligand π Bonding in Potentially Noninnocent Ligands. *Inorg. Chem* 2012, 51, 1251–1260. [PubMed: 22260321]
- (11). Bittner MM; Kraus D; Lindeman SV; Popescu CV; Fiedler AT Synthetic, Spectroscopic, and DFT Studies of Iron Complexes with Iminobenzo(semi)quinone Ligands: Implications for o-Aminophenol Dioxygenases. *Chem.-Eur. J* 2013, 19, 9686–9698. [PubMed: 23744733]
- (12). (a)Wang C-C; Chang H-C; Lai Y-C; Fang H; Li C-C; Hsu H-K; Li Z-Y; Lin T-S; Kuo T-S; Neese F; Ye S; Chiang Y-W; Tsai M-L; Liaw W-F; Lee W-Z A Structurally Characterized Nonheme Cobalt-Hydroperoxo Complex Derived from Its Superoxo Intermediate via Hydrogen Atom Abstraction. *J. Am. Chem. Soc* 2016, 138, 14186–14189. [PubMed: 27726348] (b)Oddo F; Chiba Y; Nakazawa J; Ohta T; Ogura T; Hikichi S Characterization of Mononuclear Non-heme Iron(III)-Superoxo Complex with a Five-Azole Ligand Set. *Angew. Chem., Int. Ed* 2015, 54, 7336–7339.(c)Corona T; Padamati SK; Acuna-Pares F; Duboc C; Browne WR; Company A Trapping of superoxido cobalt and peroxido dicobalt species formed reversibly from Co^{II} and O₂. *Chem. Commun* 2017, 53, 11782–11785.(d)Gordon JB; Vilbert AC; Siegler MA; Lancaster KM; Moenne-Loccoz P; Goldberg DP A Nonheme Thiolate-Ligated Cobalt Superoxo Complex: Synthesis and Spectroscopic Characterization, Computational Studies, and Hydrogen Atom Abstraction Reactivity. *J. Am. Chem. Soc* 2019, 141, 3641–3653. [PubMed: 30776222] (e)Fischer AA; Lindeman SV; Fiedler AT Spectroscopic and computational studies of reversible O₂ binding by a cobalt complex of relevance to cysteine dioxygenase. *Dalton Trans* 2017, 46, 13229–13241. [PubMed: 28686274] (f)Jones RD; Summerville DA; Basolo F Synthetic oxygen carriers related to biological systems. *Chem. Rev* 1979, 79, 139–79.
- (13). (a)Barbaro P; Bianchini C; Mealli C; Meli A Synthetic models for catechol 1,2-dioxygenases. Interception of a metal catecholate-dioxygen adduct. *J. Am. Chem. Soc* 1991, 113, 3181–3. (b)Dutta S; Peng S-M; Bhattacharya S Ligand Control on Molecular Oxygen Activation by Rhodium Quinone Complexes. *Inorg. Chem* 2000, 39, 2231–2234. [PubMed: 12526540]
- (14). Rettenmeier CA; Wadepohl H; Gade LH Structural Characterization of a Hydroperoxo Nickel Complex and Its Autoxidation: Mechanism of Interconversion between Peroxo, Superoxo, and Hydroperoxo Species. *Angew. Chem., Int. Ed* 2015, 54, 4880–4884.
- (15). Abakumov GA; Poddel'sky AI; Grunova EV; Cherkasov VK; Fukin GK; Kurskii YA; Abakumova LG Reversible binding of dioxygen by a non-transition-metal complex. *Angew. Chem., Int. Ed* 2005, 44, 2767–2771.
- (16). Kovaleva EG; Lipscomb JD Crystal structures of Fe²⁺ dioxygenase superoxo, alkylperoxo, and bound product intermediates. *Science* 2007, 316, 453–457. [PubMed: 17446402]
- (17). Cao L; Dong G; Lai W Reaction Mechanism of Cobalt-Substituted Homoprotocatechuate 2,3-Dioxygenase: A QM/MM Study. *J. Phys. Chem. B* 2015, 119, 4608–4616. [PubMed: 25751616]

Figure 1.

Left: Schematic drawing of [Co(Tp^{R2})(tBu²APH)] (**1** and **2**). Right: X-ray crystal structure of **2**.

Figure 2.

(a) UV-vis absorption spectra of **1** and **1^{ox}** in CH_2Cl_2 at 20 °C. (b) Selected bond distances (Å) for the ^tBu₂APH and ^tBu₂ISQ ligands in X-ray structures of **1** and **1^{ox}**, respectively.

Figure 3.

(a) UV-vis absorption spectrum of **2-O₂** obtained by reaction of **2** with O₂ in THF at -70 °C. [2]_{initial} = 1.25 mM. (b) X-band EPR spectrum (red) of **2-O₂** in frozen THF at 77 K. Parameters for the simulated spectrum (gray) are provided in the SI.

Figure 4.

(a) UV-vis spectral changes for the thermal interconversion of 2^{ox} (black) and **3** (red) in CH_2Cl_2 in the presence of O_2 . $[Co] = 0.7$ mM (b) Ellipsoid plot derived from the X-ray structure of **3**. Selected bond lengths (Å) are provided in red.

Scheme 1.
Proposed Mechanism of Ring-Cleaving Dioxygenases

Scheme 2.

Species Generated by Reaction of Complexes 1 and 2 with O_2