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Oxygen Activation by Co(II) and a Redox Non-Innocent Ligand: Spectroscopic Characterization of a Radical−Co(II)−Superoxide Complex with Divergent Catalytic Reactivity

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Supporting Information

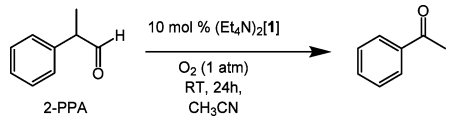
ABSTRACT: Bimetallic $(Et_4N)_2[Co_2(L)_2]$, $(Et_4N)_2[\mathbf{1}]$ (where $(L)^{3-}$ = $(N(o\text{-}PhNC(O)^iPr)_2)^{3-}$) reacts with 2 equiv of O_2 to form the monometallic species $(Et_4N)[Co(L)O_2]$, $(Et_4N)[\mathbf{3}]$. A crystallographically characterized analog $(Et_4N)_2[Co(L)CN]$, $(Et_4N)_2[\mathbf{2}]$, gives insight into the structure of $[\mathbf{3}]^{1-}$. Magnetic measurements indicate $[\mathbf{2}]^{2-}$ to be an unusual high-spin Co^{II}-cyano species (S = 3/2), while IR, EXAFS, and EPR spectroscopies indicate $[\mathbf{3}]^{1-}$ to be an end-on superoxide complex with an S = 1/2 ground state. By X-ray spectroscopy and calculations, $[\mathbf{3}]^{1-}$ features a high-spin Co^{II} center; the net S = 1/2 spin state arises after the Co electrons couple to both the $O_2^{\bullet-}$ and the aminyl radical on redox non-innocent $(L^{\bullet})^{2-}$. Dianion $[\mathbf{1}]^{2-}$ shows both nucleophilic and electrophilic catalytic reactivity upon activation of O_2 due to the presence of both a high-energy, filled O_2^- π^* orbital and an empty low-lying O_2^- π^* orbital in $[\mathbf{3}]^{1-}$.

Synthetic cobalt complexes have been known to bind O_2 since the days of Werner.[1] Upon O_2 addition, most Co^{II} complexes form kinetically inert low-spin Co^{III} terminal superoxide or μ-peroxide compounds that are inactive in catalysis.[2] Catalytic reactivity can be coaxed from such molecules by addition of a coreductant.[2i,3] In contrast, nature uses multiple metal centers[4] or redox non-innocent ligands[5] to supply the requisite electrons when activating O_2 for catalysis with first-row transition-metal complexes.

We recently reported[6] the dimeric pseudotetrahedral Co^{II} complex $(Et_4N)_2[Co_2(L)_2]$, $(Et_4N)_2[\mathbf{1}]$ (where L = $(N(o\text{-}PhNC(O)^iPr)_2)^{3-}$), which is unique among Co^{II} compounds for its ability to activate O_2 toward electrophilic O-atom transfer without supplemental coreductants. This O_2 activation proceeds with dioxygenase stoichiometry.[6] Here, we explore additional reactivity and offer insights into the O_2 activation step for this catalyst by characterizing the intermediate formed upon its interaction with O_2. Our discussion is facilitated by comparison to a stable compound formed using CN^- as an O_2 analog. Surprisingly, instead of forming a kinetically inert, low-spin Co^{III} species, we show that the Co^{II} centers remain high-spin when either substrate is added. Consequently, we argue that O_2 reduction occurs via one-electron oxidation of L rather than Co.

In addition to its behavior as a catalyst for aerobic O-atom transfer,[6] we have now found $(Et_4N)_2[\mathbf{1}]$ to be an excellent catalyst for the aerobic deformylation of 2-phenylpropionaldehyde (2-PPA), forming acetophenone in good yields (Scheme 1). While biological systems are known to carry out catalytic deformylation (nucleophilic) reactions using O_2,[7] synthetic aerobic deformylation catalysts have, to the best of our knowledge, not yet been reported.[8,9] Metal-oxygen species typically show either electrophilic or nucleophilic character; this system merits study due to its electronically divergent reactivity.[10]

Scheme 1. Catalytic Aerobic Deformylation of 2-PPA by $(Et_4N)_2[\mathbf{1}]$



To better understand this divergently reactive species, 2 equiv of CN^-, an O_2 surrogate, was added to $[\mathbf{1}]^{2-}$. CN^- was found to disrupt the bimetallic core structure, yielding 2 equiv of monometallic $(Et_4N)_2[Co(L)CN]$, $(Et_4N)_2[\mathbf{2}]$ (Figures 1 and S1−S3), which has been crystallographically characterized as containing a four-coordinate Co^{II} center, at the border between pseudosawhorse and pseudotetrahedral geometry (τ_δ = 0.59).[11] The L ligand backbone undergoes a structural rearrangement upon reaction of $(Et_4N)_2[\mathbf{1}]$ with CN^- such that each $(L)^{3-}$ ligand coordinates to a single Co center in a novel tridentate pincer-like coordination mode.[6]

Several spectroscopic techniques were employed to determine the first observable catalytically relevant intermediate responsible for the divergent reactivity of $[\mathbf{1}]^{2-}$. Gas-uptake experiments indicate that $[\mathbf{1}]^{2-}$ reacts with O_2 in a 1:2 stoichiometry (see SI), suggesting that one molecule of O_2 is taken up per Co center. UV−vis spectroscopy shows isosbestic behavior, indicating clean conversion of $[\mathbf{1}]^{2-}$ to $[\mathbf{3}]^{1-}$ via a

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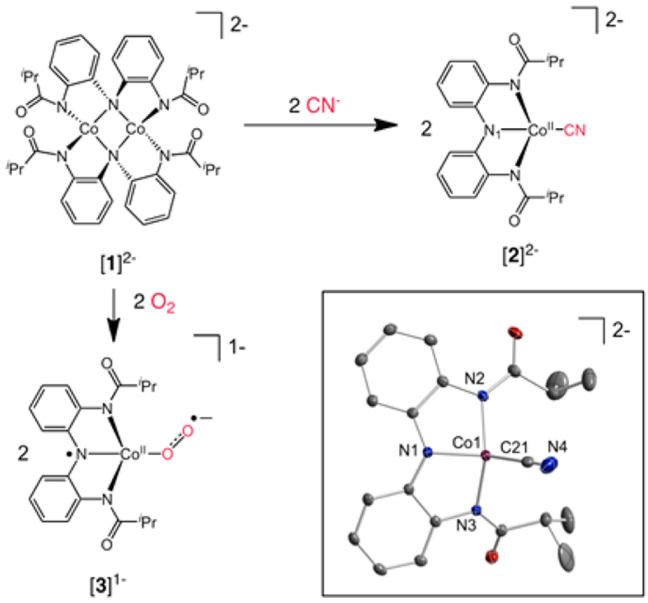

Figure 1. Preparation of $[2]^{2-}$ and $[3]^{1-}$ from $[1]^{2-}$. Thermal ellipsoid plot of $[2]^{2-}$ is shown at the 45% probability level, with H atoms and counter cations omitted for clarity.

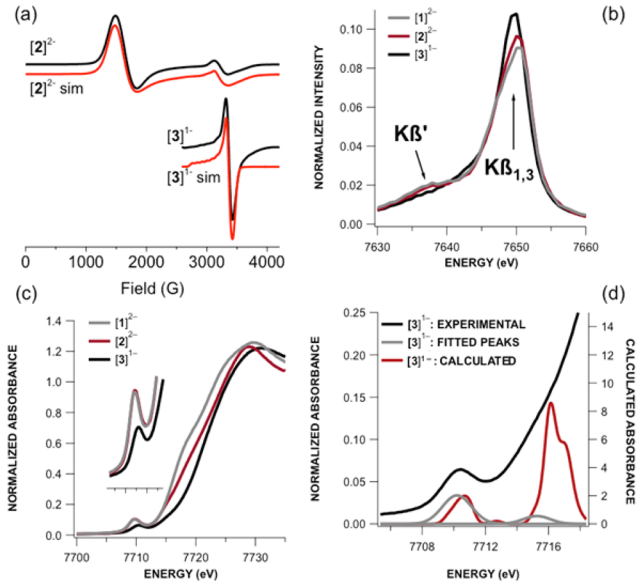

Figure 2. (a) Experimental EPR data and simulations for $[2]^{2-}$ and $[3]^{1-}$. (b) Co Kβ XES main lines of $[1]^{2-}$–$[3]^{1-}$. (c) Co K-edge XANES of $[1]^{2-}$–$[3]^{1-}$. Inset: Magnification of the Co 1s → (Co 3d + L) pre-edge features. (d) Overlay of calibrated TDDFT-calculated (B3LYP/def2-TZVP-ZORA) Co K-edge XANES pre-edge peaks for $[3]^{1-}$.

short-lived intermediate (Figure S4). The resulting burgundy species $[3]^{1-}$ can be isolated or used in situ to perform stoichiometric oxidations with PPh_3 and 2-PPA, generating the same products of catalytic oxidations using $[1]^{2-}$ (see SI). Along with the monometallic structure of $(Et_4N)_2[2]$, this result suggests that $[1]^{2-}$ reacts with O_2 to form a monometallic Co–O_2 species, $[Co(L)O_2]^{1-}$, $[3]^{1-}$. The monomeric nature of $[3]^{1-}$ is further supported by MALDI-TOF mass spectrometry, which shows that new ions with m/z = 410.49 or 412.47 amu are produced when $[1]^{2-}$ reacts with 2 equiv of $^{16}O_2$ or $^{18}O_2$, respectively (Figure S5). These mass values are consistent with formulations as $[3 - {}^{16/18}O]^-$ species, similar to mass spectral data observed for a recently reported five-coordinate Co–O_2 complex capable of C–H bond activation via a postulated Co^{IV}–oxo intermediate.[12] Liquid-cell IR techniques show that $[3]^{1-}$ has an O_2 stretching feature at 1248 cm^{-1}, which shifts to 1203 cm^{-1} upon $^{18}O_2$ labeling (Figure S6). These data are consistent with end-on Co–superoxide coordination.[13]

This molecular geometry is further supported by analysis of extended X-ray absorption fine structure (EXAFS) in the Co K-edge XAS of $[2]^{2-}$ and $[3]^{1-}$ (Figures S7–8 and Table S1). The EXAFS of $[2]^{2-}$ and $[3]^{1-}$ are qualitatively similar, yielding a Co coordination number of four with average Co–L distances of 1.98 and 1.88 Å, respectively. These distances are in good agreement with the crystallographic and DFT-optimized average Co–L distances of 2.01 and 2.04 Å for $[2]^{2-}$, respectively, and are also in good agreement with the calculated average Co–L distance for $[3]^{1-}$ at 1.87 Å. These results suggest a similar coordination geometry for $(L)^{3-}$ in $[2]^{2-}$ and $[3]^{1-}$, further indicating a monometallic Co(L) end-on superoxide structural unit for $[3]^{1-}$.

Ground-state electronic configurations of $[2]^{2-}$ and $[3]^{1-}$ were established from their magnetic properties. For $[2]^{2-}$, the μ_{eff} value of 4.27(3) μ_B at 298 K in $CDCl_3$ is indicative of an S = 3/2 ground state. EPR data (Figure 2a) confirm this unusual high-spin state, with observed (effective) g values of g_x = 4.53, g_y = 3.97, and g_z = 1.95, indicating $D > h\nu$. Despite the clear indication of an S = 3/2 ground state for $[2]^{2-}$, the EPR spectrum for $[3]^{1-}$ is surprisingly characteristic of an S = 1/2 species, best simulated by g_x = 2.20, g_y = 2.00, g_z = 1.975 (μ_{eff} = 2.13 μ_B at 298 K in CH_3CN). The observation of a "high-spin" complex of cyanide, a strong-field ligand, is unusual[14] but consistent with the low coordination number. Even more unusual is that the weaker field O_2^- complex, $[3]^{1-}$, appears low spin. Co Kβ X-ray emission spectra (XES) of $[2]^{2-}$ and $[3]^{1-}$ were measured as a probe of the local spin at Co (Figure 2b). Splitting of Kβ (3p → 1s) main lines into Kβ' and K$\beta_{1,3}$ features is a useful metric of spin population since electron delocalization out of metal 3d orbitals results in attenuation of the 3d–3p exchange energy.[15] Kβ main line splitting is markedly decreased in $[3]^{1-}$ compared to $[1]^{2-}$ and $[2]^{2-}$, consistent with a decreased local Co spin population in $[3]^{1-}$.

To defuse this spin-state conundrum, DFT calculations were employed to produce an electronic structure picture consistent with the aggregate structural and spectral data. To this end, we evaluated multiple electronic configurations for $[2]^{2-}$ and $[3]^{1-}$.[16] The quartet state for $[2]^{2-}$ was energetically favored over the doublet state by 26.7 kJ/mol, in agreement with the EPR data and the similarity of the Co X-ray absorption near-edge spectroscopy (XANES) pre-edge energy of $[2]^{2-}$ with that of $[1]^{2-}$, for the Co^{II} centers in $[1]^{2-}$ are high-spin[6] (Figure 2c). The optimized geometry for $[2]^{2-}$ as a quartet is also a superior match to the crystallographic data (Table S5). Additionally, the cyanide C≡N stretch predicted to occur at 2211 cm^{-1} is experimentally measured at 2109 cm^{-1}, in decent agreement given the well-known tendency for DFT to overestimate vibrational frequencies.[17]

For $[3]^{1-}$, DFT calculations support an S = 1/2 end-on superoxide species as the configuration with lowest energy (Table S6),[18] in accord with experimental data. For this species, a spin-coupled electronic structure is obtained. There are two low-lying doubly occupied Co-centered e-type orbitals of the pseudotetrahedral Co d orbital manifold and three singly

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occupied orbitals for the t_2-derived set (Figures 3 and S13). The superoxide ligand has two π^* valence orbitals—doubly

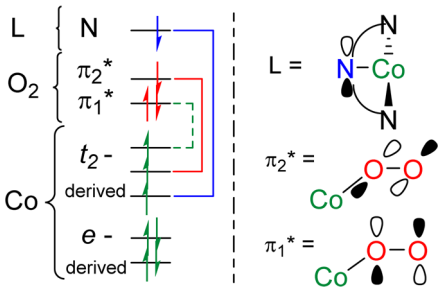

Figure 3. Molecular orbital interactions for $[\mathbf{3}]^{1-}$. (Left) Green, red, and blue arrows represent electrons in Co-, O_2-, and ligand-based orbitals, respectively. The red and blue brackets show antiferromagnetic coupling between the O_2- and N-based ligands with Co d electrons. The green dashed bracket shows the three-electron σ interaction between a Co electron and the π_1^* of the O_2^- ligand. (Right) Representation of ligand- and O_2-based orbitals.

occupied π_1^* and singly occupied π_2^*—that interact with the Co t_2-derived orbitals. The π_1^* orbital engages in a three-electron σ interaction with one Co orbital, while the π_2^* unpaired electron is coupled with another Co electron. A second antiferromagnetic interaction exists between the third Co t_2-derived electron and a ligand-based orbital having significant character from the central N atom of L. Therefore, as with $[\mathbf{2}]^{2-}$, the metal center in $[\mathbf{3}]^{1-}$ contains a high-spin $S = 3/2$ Co^{II} center. In this case, however, two of the three unpaired electrons of the Co^{II} center couple with an L radical and a superoxide radical to yield an overall $S = 1/2$ ground state. This electronic structure explains the divergent reactivity of $(Et_4N)[\mathbf{3}]$ (vide supra), for the half-filled O_2 π_2^* orbital can be either a donor orbital for nucleophilic reactivity or an acceptor orbital for electrophilic reactivity.

The Co K-edge XANES of $[\mathbf{1}]^{2-}$–$[\mathbf{3}]^{1-}$ (Figure 2c) deserve further comment. All of the other experimental and computational data clearly indicate that the Co^{II} oxidation state remains constant throughout this series, but the pre-edge features in the spectra of $(Et_4N)_2[\mathbf{1}]$ and $(Et_4N)_2[\mathbf{2}]$ effectively superimpose at 7709.7 eV, while that for $[\mathbf{3}]^{1-}$ is shifted in energy to 7710.2 eV. Furthermore, rising edges distinguish all three compounds from one another, at 7716 eV, 7717.4 eV, and 7720.4 eV for $[\mathbf{1}]^{2-}$, $[\mathbf{2}]^{2-}$, and $[\mathbf{3}]^{1-}$, respectively (Figure S9).

TD-DFT analysis of XANES pre-edge features, accomplished via calibration to a set of model compounds (Figure S10), was performed to reconcile the XANES features with the electronic structures of $[\mathbf{1}]^{2-}$–$[\mathbf{3}]^{1-}$. For $[\mathbf{2}]^{2-}$, this led to a straightforward assignment of the pre-edge transition as arising from the Co 1s to the valence "t_2"-derived set. In the case of $[\mathbf{3}]^{1-}$ (Figure 2d), the acceptor orbitals participating in this excitation have substantial O–O π^* admixture. Comparison of the spin density plots of $[\mathbf{2}]^{2-}$ vs $[\mathbf{3}]^{1-}$ shows this effect quite clearly; while the spin density in $[\mathbf{2}]^{2-}$ is highly localized on the metal center with orbitals having roughly 70% metal character, the spin for $[\mathbf{3}]^{1-}$ is more delocalized, and the orbitals are closer to 50% metal in character (Figure S11).

This delocalization of electron density manifests in the calculated Co atomic charges 0.47, 0.55, and 0.64 for $[\mathbf{1}]^{2-}$, $[\mathbf{2}]^{2-}$, and $[\mathbf{3}]^{1-}$, respectively. These values correlate to a reasonable degree ($R^2 = 0.94$) with the corresponding rising edge inflection points (Figure S9). Moreover, the trend line extrapolates to 7706 ± 3 eV at a charge of 0, consistent with the rising edge inflection of Co metal (7709 eV). Consequently, variations in the XANES of $[\mathbf{3}]^{1-}$ from the other compounds do not necessarily reflect a change in the physical oxidation state at Co after reaction with O_2. The difference in energy of the Co K-edge XANES pre-edge features is due to a difference in the nature of the acceptor orbital when comparing $[\mathbf{1}]^{2-}$ and $[\mathbf{2}]^{2-}$ to $[\mathbf{3}]^{1-}$, as has been seen previously for Cu complexes.[19] The shift to higher energy of the rising edge inflection point in $[\mathbf{3}]^{1-}$ likely reflects the highly covalent interaction of Co with an electronegative O-donor. Although XANES is widely used as a metric of physical oxidation states of transition-metal complexes, we emphasize here that the nature of the coordinated ligands also has a strong influence over the spectral profiles.

In summary, the reaction of $[\mathbf{1}]^{2-}$ with 2 equiv of CN^- yields the unusual, high-spin Co^{II} complex $[\mathbf{2}]^{2-}$, which provides structural insight toward the catalytically relevant intermediate $[\mathbf{3}]^{1-}$. Compound $[\mathbf{3}]^{1-}$ is determined to be a monometallic Co^{II}–superoxide complex supported by the redox non-innocent ligand L in its singly oxidized radical form. The local spin state of Co^{II} is $S = 3/2$, but these electrons couple with unpaired electrons on L as well as the O_2^- ligand to yield an overall $S = 1/2$ state, as seen via EPR spectroscopy. The catalytic utility of $[\mathbf{3}]^{1-}$ is therefore attributable to its redox non-innocent L supporting ligand, allowing Co to remain high-spin upon activation of O_2 and avoiding the kinetic quagmire that is a low-spin Co^{III} complex.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.5b12643.

Crystallographic data for $[\mathbf{2}]^{2-}$ (CIF)
Synthetic and spectroscopic methods, full MO diagrams, Cartesian coordinates (PDF)

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Notes

The authors declare no competing financial interest.

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