A merit of UVRR spectroscopy is that it is possible to investigate the opsin molecule, but not the retinal chromophore, in detail under physiological conditions, The present study has shown some characteristics of LA-bR and DA-bR semiquantitatively. More studies are in progress in our laboratory, including time-resolved spectroscopy on the opsin molecule in the photocycle.

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Registry No. H-Trp-OH, 73-22-3; H-Tyr-OH, 60-18-4.

Crystal Structure of a Side-On Superoxo Complex of Cobalt and Hydrogen Abstraction by a Reactive Terminal Oxo Ligand

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The activation of dioxygen by coordination to a metal center is a venerable and yet elusive goal of research in oxidation catalysis.[1] Most available evidence suggests that bound dioxygen itself is not very reactive, while metal oxo species derived therefrom often are.[2] Thus an obvious and appealing approach to O_2 activation is shown in eq 1. Much precedent exists for all of the

$$2M + O_2 \rightarrow MO_2 + M \rightarrow MOOM \rightarrow 2M{=}O \qquad (1)$$

intermediate species depicted, but there are few examples of the whole sequence of conversions,[3] Herein we report on a cobalt complex that binds dioxygen in an unprecedented manner and eventually yields products implying a reactive cobalt oxo intermediate,

Magnesium reduction of the readily available cobalt halides Tp′Co^{II}X (Tp′ = hydridotris(3-*tert*-butyl-5-methylpyrazolyl)borate, X = Cl, I; THF solvent)[4] in a nitrogen atmosphere yielded the dinitrogen complex Tp′Co(N_2) in 55% isolated yield (see Scheme I). The IR spectrum of this compound exhibited ν_{NN} at 2046 cm^{-1} (KBr), and dissolution in degassed CH_2Cl_2 resulted in the release of 1,0 equiv of N_2 (measured with a Toepler pump) and quantitative reisolation of Tp′CoCl. The ^{1}H NMR spectrum of Tp′Co(N_2) exhibited isotropically shifted resonances expected of the tris(pyrazolyl)borate ligand (δ(C_6D_6): −7.3 (27 H), 16.7 (9 H), 27.5 (1 H), 39.8 (3 H) ppm), and the magnetic susceptibility showed Curie behavior of a simple paramagnet with an effective magnetic moment of 3.87 μ_B at room temperature.[5] This is consistent with the two unpaired electrons of a tetrahedral Co(I) complex augmented by a significant orbital contribution.

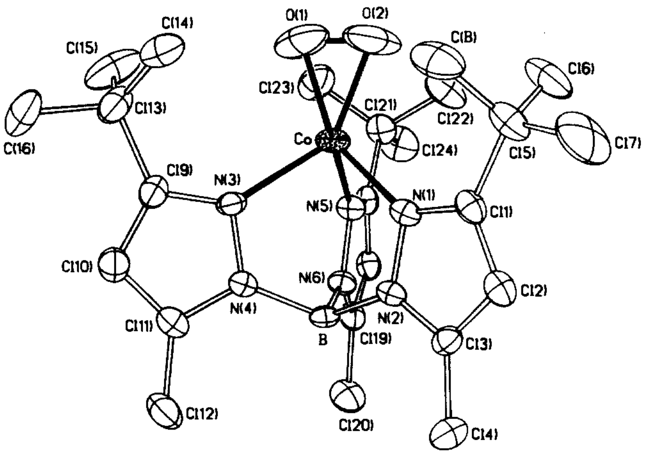
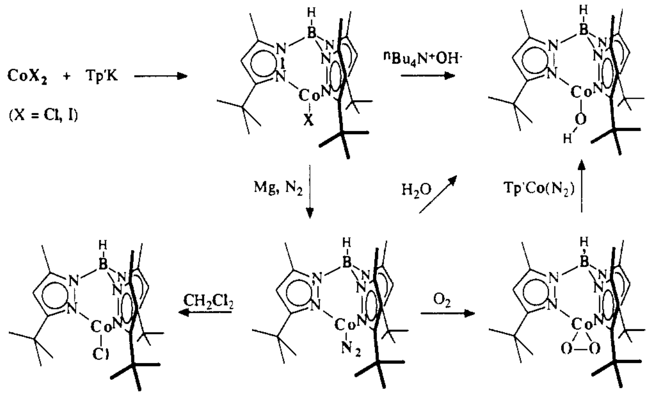


Figure 1. The molecular structure of Tp′Co(O_2). Selected bond distances: Co–O(1), 1.816 (5) Å; Co–O(2), 1.799 (6) Å; O(1)–O(2), 1.262 (8) Å; Co–N(1), 2.008 (4) Å; Co–N(3), 2.042 (4) Å; Co–N(5), 2.069 (4) Å. Interatomic angles: O(1)–Co–O(2), 40.9 (3)°; N(1)–Co–N(3), 91.6 (2)°; N(1)–Co–N(5), 92.1 (2)°; N(3)–Co–N(5), 92.9 (1)°.

Scheme I



Exposure of a pentane suspension of Tp′Co(N_2) to an excess of dioxygen immediately yielded the dioxygen complex Tp′Co(O_2), which was purified by filtration through Florisil and recrystallization from hot toluene (44% isolated yield).[6] The IR spectrum of this compound exhibited a new band (assigned as ν_{OO}) at 961 cm^{-1}. Whereas the O–O stretching vibration is generally used to classify dioxygen complexes into superoxo-containing (1200–1070 cm^{-1}) or peroxo-containing (930–740 cm^{-1}) species,[7] this criterion obviously fails in the case at hand. Therefore the molecular structure of Tp′Co(O_2) was determined by X-ray diffraction (see Figure 1).[8]

The crystal consists of isolated molecules featuring cobalt in the embrace of the sterically hindered tridentate nitrogen ligand, The fourth and last coordination site left by this "tetrahedral

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(5) The susceptibility data was fitted with a Curie–Weiss expression ($\chi_m = [C/(T - \theta)] + \mathrm{TIP}$). C = 1.59 emu K/mol, θ = 2.1 K, TIP = 6.91 × 10^{-4} emu.

(6) Tp′Co(O_2): ^{1}H NMR (C_6D_6) δ −2.1 (s, 27 H), 9.5 (br s, 1 H), 18.2 (s, 9 H), 33.6 (s, 3 H); IR (KBr) 2543, 2523 (ν_{B-H}), 961 (ν_{O-O}) cm^{-1}; UV–vis (THF) 321 (ϵ = 1286), 365 (1033) nm; mp 206–208 °C dec. Anal. Calcd for $C_{24}H_{40}BCoN_6O_2$: C, 56.02; H, 7.85; N, 16.34. Found: C, 56.52; H, 7.74; N, 16.40.

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enforcer" is occupied by the dioxygen ligand, which is coordinated in a side-on fashion. The oxygen–oxygen distance of 1.262 (8) Å clearly resolves the ambiguity between a Co^{III}–peroxo and a Co^{II}–superoxo description of the bonding in favor of the latter.[9] While there are many structurally characterized superoxo complexes, $Tp'Co(O_2)$ seems to feature the first example of a symmetrically side-on bound superoxide.[10] Kitajima et al. have recently described a doubly side-on bound peroxide ligand (μ-η^2:η^2-O_2^{2-}) coordinated to two tris(pyrazolyl)borate copper fragments.[11] Thus it appears that metals in this particular coordination environment generally favor side-on coordination of O_2 (and possibly other ligands).[12]

To further characterize this unusual O_2 complex, $Tp'Co(N_2)$ was exposed to a mixture of $^{16}O_2$, $^{16}O^{18}O$, and $^{18}O_2$ (1.0:1.87:1.1, determined by mass spectrometry). The IR spectrum of the resulting mixture of dioxygen complexes exhibited three bands at 961, 937, and 908 cm^{-1}. This is the expected pattern for a side-on complex,[13] whereas end-on complexes should exhibit four bands (due to the $M{-}^{16}O^{18}O/M{-}^{18}O^{16}O$ isomerism).[14] The magnetic susceptibility of $Tp'Co(O_2)$ was measured on a Faraday balance in the temperature interval 4–270 K. The compound is paramagnetic and has a temperature-independent effective magnetic moment of 3.88 μ_B (extrapolated to 298 K).[15] Tetrahedral cobalt(II) usually exhibits magnetic moments in the range of 4.6–4.8 μ_B, due to the spin-only moment of three unpaired electrons plus a sizable orbital contribution.[16] The superoxide ion is an odd-electron species with a magnetic moment of 1.89 μ_B.[17] The observed moment of $Tp'Co(O_2)$ is consistent with strong antiferromagnetic coupling of the metal ion ($S = {}^3/_2$) and the superoxide ligand ($S = {}^1/_2$),[18] resulting in a ground state with $S = 1$ to which is added a significant orbital contribution.

We were initially puzzled by the observation that reactions of $Tp'Co(N_2)$ with stoichiometric amounts of dioxygen yielded significant quantities of Tp'CoOH[19] as a side product even in rigorously dried solvents. Eventually, we found that addition of 1 equiv of $Tp'Co(O_2)$ to a solution of $Tp'Co(N_2)$ resulted in the formation of Tp'CoOH in 90% yield by NMR (based on total Tp'Co). When this reaction was carried out in toluene-d_8, no incorporation of deuterium into the hydroxyl group could be detected by IR spectroscopy. However, examination of the hydroxide complex by mass spectroscopy indicated some incorporation of deuterium in the *tert*-butyl groups of the tris(pyrazolyl)borate ligand. This observation suggests abstraction of a hydrogen from the ligand followed by deuterium atom abstraction from solvent as one reaction pathway. Further experiments to identify the source of the hydrogen atom are currently in progress.

The first step in this reaction most likely involves displacement of N_2 from $Tp'Co(N_2)$ by $Tp'Co(O_2)$ and formation of a dinuclear peroxo bridged cobalt complex. The severe steric demands of the Tp' ligand may further destabilize the already weak O–O bond in the peroxide intermediate,[20] leading to bond homolysis. The resultant cobalt oxo complex is expected to display high reactivity.[21] Its ability to abstract hydrogen atoms suggests a description as $Tp'Co^{II}{-}O^{\bullet}$, i.e., an oxygen atom radical bound to a metal atom or oxide monoanion (O^-). We note that such species are thought to be important in the oxidative coupling of methane over metal oxides at elevated temperatures.[22] Efforts to modify our system to direct the attack of the oxygen atom at external substrates rather than the ligand are currently under way.

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Supplementary Material Available: Tables of X-ray structure determination of $Tp'Co(O_2)$ including crystal data, atomic coordinates and isotropic thermal parameters, and bond distances and angles (7 pages). Ordering information is given on any current masthead page.

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True Nature of Trihalotris(tetrahydrofuran)molybdenum(III), $MoX_3(THF)_3$ (X = Cl, Br, I). A Paramagnetic ^1H Nuclear Magnetic Resonance Study[†]

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$MoCl_3(THF)_3$ is extensively used for the synthesis of molybdenum complexes in the III and lower oxidation states.[1-5] Several improved preparation procedures[6-8] have been subsequently published after the original report.[9] However, its structural nature

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[†] Dedicated to Prof. Fausto Calderazzo on the occasion of his 60th birthday.

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