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Addition of Superoxide Radical Anion to Cobalt(II) Macrocyclic Complexes in Aqueous Solution

Sir:

The superoxide radical anion, $\cdot O_2^-$, is apparently of immense consequence in biological systems, its elimination being catalyzed by superoxide dismutase, SOD, a metalloenzyme.[1] The uncatalyzed disproportionation reaction

$$2\cdot O_2^- \xrightarrow{2H^+} H_2O_2 + O_2$$

is very slow ($k \sim 10^2\ M^{-1}\ s^{-1}$) although the corresponding reaction of $\cdot O_2^-$ with its conjugate acid, $\cdot O_2H$ (pK_a 4.8), is quite rapid ($k = 8.5 \times 10^7\ M^{-1}\ s^{-1}$).[2] The reported aqueous chemistry of $\cdot O_2^-$ has been exclusively oxidation-reduction[3,4] although there remains a controversy about the possible deleterious effects of $\cdot O_2^-$ in complex biochemical systems inasmuch as simple reversible redox reactions cannot lead to biological damage.[3] To date, no evidence has been advanced for nonredox reactions of $\cdot O_2^-$ in aqueous solution although some have been proposed in the past.[5] In this paper we report the addition of $\cdot O_2^-$ to some Co(II) complexes containing macrocyclic ligands as demonstrated by use of the fast kinetics pulse radiolysis technique.

The pulse radiolysis apparatus (time resolution < 1 μs) at the U.S. Army Natick Laboratories[6] and the radiolysis technique for generating selected free radicals[7] have been amply described in detail. The macrocyclic complexes used in this study, $[Co(4,11\text{-dieneN}_4)(H_2O)_2{}^{2+}$, $Co(1,3,8,10\text{-tetraeneN}_4)(H_2O)_2{}^{2+}$, $Co(1,3,8,10\text{-tetraeneN}_4)(H_2O)_2{}^{3+}]$,[8] were available from our laboratory reserves.[9]

In contrast to many Co(II) chelates which are sensitive to O_2, the Co(II) macrocyclic complexes used in this study are stable for modest periods of time in oxygenated neutral solution; the spectra of the complexes were not affected by the presence of O_2 during the time required (~30 min) to perform the experiments. The radiolysis of these solutions generates $\cdot O_2^-$ from the fast reactions of e_{aq}^- and H atoms with O_2; the presence of *tert*-butyl alcohol ensures the scavenging of OH radicals. Alternatively, all the primary radicals can be converted to $\cdot O_2^-$ in the presence of HCO_2^- and O_2.[3]

$$e_{aq}^- + O_2 \rightarrow \cdot O_2^- \qquad (k = 2.2 \times 10^{10}\ M^{-1}\ s^{-1})^{10}$$

$$H + O_2 \rightarrow \cdot O_2H \qquad (k = 2.2 \times 10^{10}\ M^{-1}\ s^{-1})^{11}$$

$$OH + (CH_3)_3COH \rightarrow \cdot CH_2C(CH_3)_2OH + H_2O \qquad (k = 5.2 \times 10^8\ M^{-1}\ s^{-1})^{12}$$

The reaction of both Co^{II} macrocyclic complexes with $\cdot O_2^-$ at pH 7–8 yielded the spectra of transient intermediates (Figure 1). From the formation kinetics of the transient spectra, the rate constants for reaction of $\cdot O_2^-$ with $Co^{II}(4,11\text{-dieneN}_4)$ and $Co^{II}(1,3,8,10\text{-tetraeneN}_4)$ $(CoN_4)^{2+}$ were determined to be 1.4×10^9 and $1.6 \times 10^9\ M^{-1}\ s^{-1}$, respectively. The magnitude of these rate constants rules out the participation of $\cdot O_2H$ in these reactions at the pH values of the experiments. The same spectral intermediates were obtained irrespective of the method of generating the $\cdot O_2^-$ radical. The spectrum of $\cdot O_2^-$ is also given[2] in Figure 1 for comparison. The spectra of the transient species are unquestionably not those of the corresponding Co(I)[9] or Co(III)[13] complexes thereby ruling out $\cdot O_2^-$ as a simple electron transfer agent in its reaction with Co(II). We conclude that $\cdot O_2^-$ adds to the metal center at a labile axial site[14] giving rise to a complex possessing the observed intense charge transfer bands.

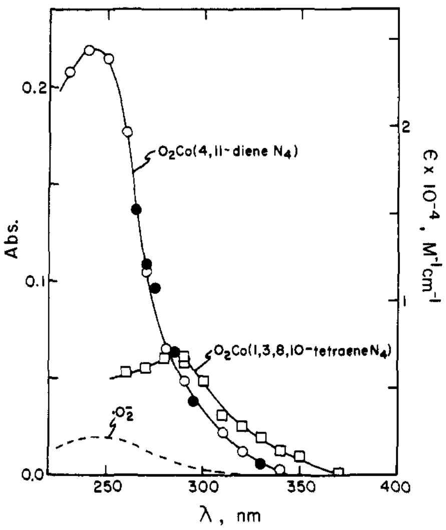

Figure 1. Transient absorption spectra produced in the pulse radiolysis of: ○, 5×10^{-5} M $Co^{II}(4,11\text{-dieneN}_4)$, 1.3×10^{-3} M O_2, 0.25 M *tert*-butyl alcohol at pH 7.1 ($Co(II) + \cdot O_2^-$ reaction): □, 4×10^{-5} M $Co^{II}(1,3,8,10\text{-tetraeneN}_4)$, 1.3×10^{-3} M O_2, 0.25 M *tert*-butyl alcohol at pH 8.0 ($Co(II) + \cdot O_2^-$ reaction); ●, 4×10^{-4} M $Co^{II}(4,11\text{-dieneN}_4)$, 5.6×10^{-5} M O_2, 0.5 M *tert*-butyl alcohol at pH 7.1 ($Co(I) + O_2$ reaction). Dose/pulse = 1.6 krad; optical path = 2 cm. The spectrum of $\cdot O_2^-$ is shown for comparison (- - -).

$$\cdot O_2^- + CoN_4{}^{2+} \rightarrow O_2CoN_4{}^+ \qquad (1)$$

It is not possible at present to establish if the products of reaction 1 are Co(II)-superoxy or Co(III)-peroxy complexes. In any event, the spectra of the adduct intermediates are not stable; they decay into more weakly but similarly absorbing species. The $O_2Co(4,11\text{-dieneN}_4)$ complex decays with $t_{1/2} \sim 1$ min with kinetics that are uncharacterizable due to the slow rate and small absorbance changes. The $O_2Co(1,3,8,10\text{-tetraeneN}_4)$ complex decayed more rapidly in a decidedly second-order manner ($k = 2.1 \times 10^3\ M^{-1}\ s^{-1}$); the formation of a binuclear μ-complex as the final product is a distinct possibility.

Figure 1 also shows that the spectrum of the $O_2Co(4,11\text{-dieneN}_4)$ complex also arises from the reaction of $Co^I(4,11\text{-dieneN}_4)$ with O_2. Under the experimental conditions shown, e_{aq}^- reduces Co(II) to Co(I) ($k = 4.4 \times 10^{10}\ M^{-1}\ s^{-1}$) and O_2 subsequently reacts with the Co(I) complex ($k_2 = 1.7 \times 10^9\ M^{-1}\ s^{-1}$).[9] Thus, the O_2-addition mechanism suggested previously[9] for Co^I-macrocyclic complexes is now unequivocally established:

$$O_2 + CoN_4{}^+ \rightarrow O_2CoN_4{}^+ \qquad (2)$$

The magnitude of k_2 and the time frame for reaction 2 (10–30 μs) rule out dimer formation as a primary process even if it is assumed that $k \sim 10^9\ M^{-1}\ s^{-1}$ for the dimerization of the monomer.

In contrast, O_2 does not form an adduct to $Co_{aq}{}^+$, but rather oxidizes it, and $\cdot O_2^-$ does not react with $Co_{aq}{}^{2+}$.[15] We have also observed that $\cdot O_2^-$ adds to $Co(bpy)_2^{2+}$ ($k = 1.9 \times 10^6$ $M^{-1}\,s^{-1}$). However, no reaction was observed between $\cdot O_2^-$ and Co^{III}(1,3,8,10-tetraeneN$_4$) or Cu^{II}(4,11-dieneN$_4$)[16] ($k < 10^5\ M^{-1}\,s^{-1}$).

The observation that $\cdot O_2^-$ adds irreversibly to certain metal complexes requires that this reaction be included when consideration is given to the role of $\cdot O_2^-$ in the damage of biological systems. Observation of growth of obligate anaerobes, which do not contain SOD, under aerobic conditions[17] in the presence of added Co^{2+} appears to suggest the possible interaction of $\cdot O_2^-$ and cellular Co(II) complexes. Consideration should be given to the possibility of reaction of $\cdot O_2^-$ and vitamin B_{12} precursors which can lead to severe deficiency of B_{12} triggered by disorders in SOD levels.

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The Structure of 1-Bromo-1*H*-cyclobuta[*de*]naphthalene

Sir:

Recently the syntheses of the peri-bridged compounds 1-bromo-1*H*-cyclobuta[*de*]naphthalene (**1**) and 1*H*-cyclobuta[*de*]naphthalene (**2**) were reported, and their structures assigned, primarily by NMR and intuitive methods.[1] From the magnetic equivalence of its C(1) protons, **2** was surmised to be planar or to rapidly interconvert between equivalent conformers folded along C(8)-C(9).[1] We report here the crystal structure and some revealing chemistry of **1**.

Table I. Bond Distances (Å) and Angles (deg) of Interest[a]

	1[a]	Naphthalene
C(1a)-C(2)	1.356 (6)	1.361 (4)
C(2)-C(3)	1.432 (6)	1.421 (4)
C(3)-C(4)	1.381 (6)	1.361 (4)
C(4)-C(9)	1.420 (7)	1.425 (4)
C(9)-C(8)	1.382 (6)	1.410 (4)
C(1a)-C(8)	1.368 (6)	1.435 (4)
C(8)-C(1a)-C(2)	118.4 (6)	120.2 (2)
C(1a)-C(2)-C(3)	114.6 (6)	120.5 (2)
C(2)-C(3)-C(4)	124.4 (6)	120.5 (2)
C(3)-C(4)-C(9)	120.2 (6)	120.2 (2)
C(4)-C(9)-C(8)	111.1 (6)	119.2 (2)
C(9)-C(8)-C(1a)	130.7 (6)	119.2 (2)
C(4)-C(9)-C(5)	137.7 (6)	121.5 (2)
C(1a)-C(8)-C(7a)	98.7 (6)	121.5 (2)

[a] Values for chemically equivalent bonds and interbond angles have been averaged.

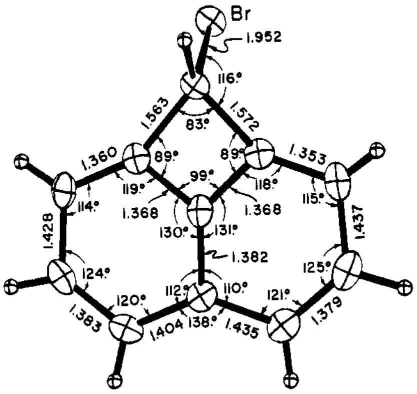
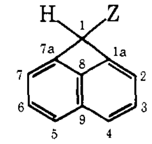


Figure 1. ORTEP diagram of the 1-bromo-1*H*-cyclobuta[*de*]naphthalene molecule. Hydrogen atoms have been reduced in size for clarity. The thermal ellipsoids are shown at the 50% probability level.



1, Z = Br   **3a**, Z = $O_3SC_6H_4CH_3$-*p*
2, Z = H   **3b**, Z = O_2CCH_3

Long colorless transparent needles of **1**, grown from toluene solution, were sealed in capillary tubes and used for cell constant[2] and space group determination[2] and for x-ray diffraction data collection, all at −60 (±5) °C. Intensity data were collected on an automated four-circle diffractometer using graphite monochromatized Mo Kα radiation. The data were corrected for absorption,[2,3] Lorentz-polarization effects and crystal decay, yielding 1717 independent *F*'s (of which 1447 were $>3\sigma$). The structure was solved by the heavy atom Patterson method and refined by standard techniques.[4] Hydrogen atoms were located using difference Fourier maps and their parameters were also refined. The *R* factor is 0.065 and the "goodness-of-fit" is 3.7.[4] All but one pair of chemically equivalent bond distances in the molecule are equal within about one standard deviation.[5]

Table I compares the dimensions of **1** and naphthalene.[6]