

## 4.7: General Aspects of the Chemistry of Dioxygen

### Redox Chemistry of Free Molecular Dioxygen

Dioxygen has a rich redox chemistry that is not explicitly exploited in the oxygen carriers, but which is central to enzymes that coordinate and activate dioxygen for subsequent reaction with a substrate. On reduction of dioxygen by one electron, the superoxide anion radical  $O_2^{\cdot-}$  is formed. Concomitant with a reduction in bond order from 2.0 to 1.5 is an increase in bond length from 1.21 to 1.30 Å. A second reduction step produces the peroxide anion  $O_2^{2-}$ ; the bond order is one, and the O—O separation is 1.49 Å. Each of these reduced species,  $O_2^{\cdot-}$  and  $O_2^{2-}$ , has a characteristic O—O stretching vibration in the infrared region. The free-energy changes and electrochemical potentials for the reduction of dioxygen at unit activity, pH = 1 ( $E^\circ$ ), are different from those at pH 7.0 ( $E^\circ'$ ), as shown in Figure 4.11.<sup>58,62</sup> The values at pH 7.0 are more relevant to physiological conditions. Note that the superoxide anion may function as either an oxidant or a reductant.

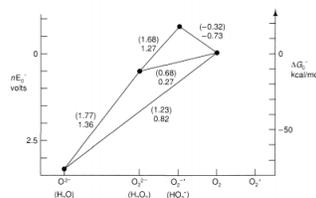


Figure 4.11 - Free-energy changes in the aqueous redox chemistry of dioxygen. Standard state  $P(O_2) = 1$ . Electrode potentials are at pH 7; those in parentheses are at unit activity.

### Geometry and Electronic Structure of Coordinated Dioxygen

In coordinating to metals, dioxygen shows a great variety of geometries and two formal oxidation states. Many complexes have  $\nu(O-O)$  values in the range 740 to 930  $cm^{-1}$ , and, where known, an O—O separation in the range 1.40 to 1.50 Å. By analogy with the peroxide anion, these species are designated peroxy,  $O_2^{II}$ . Similarly, the designation superoxy  $O_2^{I\cdot}$  is applied to those complexes where  $\nu(O-O)$  values are in the range 1075 to 1200  $cm^{-1}$ , and the O—O separation is around 1.30 Å.<sup>63</sup> Although such O—O separations and vibrations are consistent with coordinated peroxide or superoxide moieties, the net amount of charge transferred onto the dioxygen ligand from the metal and its other ligands is difficult to measure experimentally and is probably variable. Thus the oxidation state of the dioxygen ligand and that of the metal are best considered in a formal sense rather than literally—hence the use of the terminology  $O_2^I$  to indicate oxidation state I- for the  $O_2$  moiety as a unit (not each O atom). Because of the high degree of covalency in the M—O bond, a more sensible comparison, at least for the peroxy class of compounds, is with organic peroxides, ROOH or ROOR. The clear separation of coordinated dioxygen into either the superoxy or the peroxy class is shown in Figure 4.12.<sup>63-66</sup> Only those compounds for which both stretching frequencies ( $\nu(O-O)$ ) and O—O separations ( $r(O-O)$ ) are available are shown; for the purpose of the plot, non-coordinated anions and cations, replacement of ethylenediamine by two ammonia ligands, and replacement of triphenylphosphine by alkylphenylphosphines are assumed not to perturb significantly  $\nu(O-O)$  or  $r(O-O)$ .

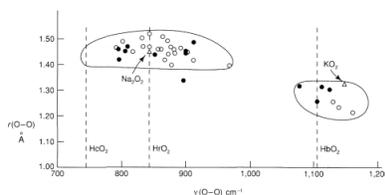


Figure 4.12 - Scatter diagram showing the distribution of O—O stretching frequencies and separations in ionic superoxides and peroxides ( $\Delta$ ) and in coordination compounds. An open circle denotes  $O_2$  coordinated to one metal; a filled circle denotes  $O_2$  bridging two metals. The O—O stretching frequencies of oxyhemoglobin, oxyhemocyanin, and oxyhemerythrin are marked by dashed lines.

At least seven different geometries have been observed for the coordination of dioxygen (Figure 4.13),<sup>63-66</sup> only three or four of which are currently known to be biologically relevant—the superoxy

$M-O-O$  (for oxyhemoglobin), the peroxy  $M-O-O-M$  or  $M-O-O-M$  (for oxyhemocyanin), and the hydroperoxy  $M-O-M-OOH$  (for oxyhemerythrin).

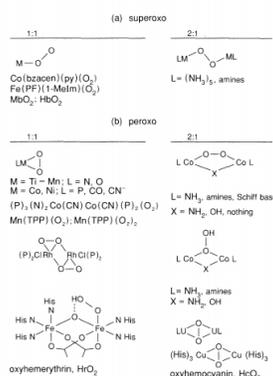


Figure 4.13 - Modes of attachment of  $O_2$  to metals. P, N, and O denote phosphine, amine, and oxygen ligands, respectively.

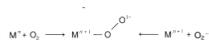
The geometry is a function of the metal, its oxidation state, and its ligands. For the late transition metals of the cobalt and nickel triads, with soft  $\pi$ -acid ligands, such as phosphines and carbonyls, and with an initially low oxidation state of the metal, triangular coordination of a peroxy species with covalent M—O<sub>2</sub> bonds is common.<sup>63</sup> Concomitant with the formal reduction of dioxygen, the metal center undergoes a formal two-electron oxidation:



In this example, where the metal has undergone, at least formally, a two-electron oxidation, the UV-visible properties of the metal-dioxygen complex tend to resemble those of bona fide  $M^{III}$  rather than  $M^I$  species.

Early transition metals (Ti, V, Cr triads) often coordinate several peroxy species, leaving the metal in formally a very high oxidation state (e.g.,  $Cr(O_2)_4^{3+}$ , a  $Cr^V$  ion).<sup>63</sup> The M—O<sub>2</sub> links have more ionic character, with the  $\eta$ -peroxy groups acting as bidentate ligands. Titanium and molybdenum(II) porphyrins bind, respectively, one and two dioxygen molecules in this manner.<sup>65</sup>

With harder  $\sigma$ -donor ligand systems, such as those containing nitrogen and oxygen donors, and the metal center in a normal oxidation state, a formal one-electron reduction to an end-on coordinated superoxy species occurs with a bent  $M-O-O$  bond. Metal-dioxygen species can also be formed by adding the superoxide anion to the oxidized species:<sup>64</sup>



(4.27)

In the absence of steric constraints, dimerization to a (bridging)  $\mu$ -peroxo species frequently occurs, especially for cobalt-dioxygen complexes:



Figure 4.12 is one such example.

These dicobalt species (right-hand side of Equation 4.28) may be oxidized by one electron to give a  $\mu$ -superoxo moiety. A clear shortening of the O—O bond and concomitant increase in the value of  $\nu(O—O)$  are observed in several superoxo-peroxo pairs. These and other modes of  $O_2$  attachment are illustrated in Figure 4.13. Some geometries are represented by only one or two examples, and some geometries, for example, a linear M—O—O species, have never been observed.

In binding to metals,  $O_2$  effectively functions both as a  $\pi$  acid, accepting into its  $\pi^*$  orbitals electron density from the filled d orbitals of the metal, and as a  $\sigma$  donor, donating electron density into an empty metal d orbital. Thus other  $\sigma$  donor or  $\pi$  acceptor ligands, such as nitric oxide (NO), alkyl isocyanides (R—NC), alkyl nitroso (R—NO), and carbon monoxide (CO), are often observed to bind to the same metal complexes that bind  $O_2$ . The nature of the metal-dioxygen linkage in biological oxygen carriers and their models will be examined in more detail later.

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