

(4.27)

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

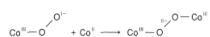


Figure 4.12 is one such example.

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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