4.6: General Aspects of the Chemistry of Copper

The chemistry of copper in biological systems is limited to oxidation states I and II. The Cu^{I} state has electronic configuration d^{10}. Unless there are ligand bands or strong ligand-to-copper charge-transfer bands, diamagnetic Cu^{I} species are colorless. Complexes of Cu^{II} (d^{9}) are often blue in color. The single unpaired electron makes Cu^{II} amenable to electron paramagnetic resonance (EPR) techniques, at least if the electron spins of Cu^{II} centers are independent of one another. In oxyhemocyanin the spins are so strongly coupled ($-J > 600\ cm^{-1}$) that at room temperature and below the system is effectively diamagnetic and the pair of Cu^{II} ions is EPR silent.[14]

In aqueous solutions the Cu^{I} ion is unstable with respect to disproportionation to Cu metal and Cu^{II} ion:[62]

$$Cu^{II} + 2e^{-} \rightleftharpoons Cu \qquad E^{o} = 0.3402V \tag{4.6.1}$$

$$Cu^{+} + e^{-} \rightleftharpoons Cu \qquad E^{o} = 0.522V \tag{4.35}$$

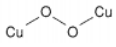
$$2Cu^{+} \rightleftharpoons Cu + Cu^{II-} \qquad E^{o} = 0.182V \tag{4.6.2}$$

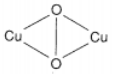
The Cu^{I} state may be stabilized by ligands, especially sulfur-containing ones, or by immobilization as afforded by a protein matrix, or in nonaqueous solvents, such as acetonitrile, in the absence of dioxygen. Whereas Cu^{I} thiolate species are stable, Cu^{II} thiolate species usually are unstable with respect to the disproportionation:[101]

$$2Cu^{II}\text{—}SR \rightarrow 2Cu^{I} + R\text{—}S\text{—}S\text{—}R \tag{4.36}$$

Again, immobilization may give kinetic stability to Cu^{II} thiolate species, as occurs in the blue-copper family of electron-transport proteins.

Copper(l) complexes are often two-coordinate with a linear arrangement of ligands. Three-, four-, and possibly five-coordinate complexes are known.

In the presence of O_2, nonbiological copper(l) [and iron(II)] complexes are often susceptible to ligand degradation, which may give the illusion of O_2 binding.[102] The mechanisms by which this reaction occurs remain essentially unknown. Iron-porphyrin systems are rather more robust. Nonetheless, there are now several well-characterized copper(l) systems that reversibly bind dioxygen,[15b,103] at least at low temperature. One that has been structurally characterized features a 

dicopper(II)-peroxo moiety,[103f] while a second, with more properties in common with oxyhemocyanin, features a 

moiety.[103g]