

## 4.5: General Aspects of the Chemistry of Cobalt

Many parallels exist between the chemistry of  $\text{Fe}^{\text{II}}$ - and  $\text{Co}^{\text{II}}$ -porphyrinato systems. Dioxygen binds to many  $\text{Co}^{\text{II}}$  complexes to give mononuclear 1:1  $\text{Co}:\text{O}_2$  complexes with a bent geometry



and dinuclear 2:1  $\text{Co}:\text{O}_2$  complexes,<sup>64,66</sup> analogous to those described for  $\text{Fe}^{\text{II}}$  systems in Reactions (4.29a) and (4.29b). Indeed, these dinuclear systems were the first nonbiological oxygen carriers to be isolated. The geometry of the dioxygen moiety, spanning two metals, may be *cis* or *trans*:



However, whereas these dinuclear cobalt species are invariably octahedral, dinuclear copper-peroxo species are tetrahedral or distorted square pyramidal.<sup>40,41</sup>

In the late 1960s, 1:1  $\text{Co}:\text{O}_2$  species were first isolated by use of a combination of low temperatures and specific Schiff-base ligands.<sup>104</sup> It was found that cobalt corrins, such as vitamin  $\text{B}_{12}$ , also formed 1:1 dioxygen adducts,<sup>105</sup> although this chemistry is not known to be utilized by living systems.<sup>103</sup> Cobalt(II) porphyrins also form 1:1 adducts but with low  $\text{O}_2$  affinity, especially in nonpolar, aprotic solvents. Thus hemoglobin and myoglobin may be reconstituted from a cobaltoheme with preservation not only of dioxygen-binding capabilities but also of cooperativity.<sup>106</sup> The synthetic 1:1  $\text{Co}:\text{O}_2$  complexes have proven to be very useful in increasing our understanding of factors that determine oxygen affinity for cobalt systems and by extrapolation for iron systems. Two important differences make  $\text{Co}^{\text{II}}$  systems more accessible. First, in contrast to iron systems, the cleavage reaction (4.29c) and redimerization to a  $\mu$ -oxo species (Reaction 4.29d) do not occur (see Figure 4.15). Thus  $\text{Co}^{\text{II}}$  complexes of  $\text{O}_2$  are stable in solution at room temperature without the need for protection illustrated in Figure 4.14. Second, for  $\text{Co}^{\text{II}}$ -porphyrinato systems, the equilibrium constant for the addition of a second axial base, such as pyridine or 1-methylimidazole, is small. Thus the disproportionation to four-coordinate and six-coordinate species that occurs for corresponding  $\text{Fe}^{\text{II}}$  systems (Reaction 4.33) does not occur. This difference simplifies the interpretation of spectral changes that are used to obtain thermodynamic and kinetic parameters of which there are now voluminous examples.<sup>66</sup>

Moreover, the 1:1  $\text{Co}-\text{O}_2$  complexes are paramagnetic. From the small  $^{59}\text{Co}$  hyperfine splitting, it is deduced that the single unpaired electron resides primarily on the dioxygen moiety.<sup>104a,105</sup> From other experiments<sup>107</sup> it is apparent that net transfer of electron density from the metal onto the dioxygen varies considerably, from about  $0.1e^-$  to about  $0.8e^-$ . For example, it is found for a given  $\text{Co}^{\text{II}}$  Schiff base,  $\text{Co}(\text{bzacen})$ , that the redox potential of the cobalt-Schiffbase center  $\text{LCo}$ , measured by cyclic voltammetry,  $E_{1/2}$ ,



is a linear function of  $\log K(\text{O}_2)$  as the axial base  $B$  is varied. The more easily the  $\text{Co}^{\text{II}}$  center may be oxidized, the higher is the  $\text{O}_2$  affinity,<sup>103</sup> as illustrated in Figure 4.18A. The dioxygen affinity also increases as the basicity of the axial nitrogenous ligand increases.<sup>104a</sup> This effect is illustrated in Figure 4.18B. Because of differing steric requirements, dimethylformamide (DMF), substituted imidazole, and piperidine (pip) ligands do not fall on the correlation defined by the series of substituted pyridine species. Note the synergistic nature of dioxygen binding: in general, the more electron density that is pumped onto the metal by the axial base, the more electron density is available for donation into the  $\pi^*$  orbitals of the dioxygen ligand.  $E_{1/2}$  and  $\log K(\text{O}_2)$  are also correlated, although more weakly, for a number of hemoglobins (Figure 4.18C).<sup>108</sup> Here the porphyrin and axial base remain constant, but presumably the surroundings of the heme group and  $\text{O}_2$  binding site vary in a manner that is less well-defined than in the model systems of Figure 4.18A and B. Notwithstanding these various perturbations to the metal center, the  $\text{O}-\text{O}$  stretch occurs at about  $1140\text{ cm}^{-1}$ , placing all 1:1 cobalt and iron-dioxygen complexes of nitrogenous and other hard ligands into the superoxo class.\*

Cobalt(II) porphyrins and their adducts with diamagnetic molecules invariably have spin  $S = \frac{1}{2}$ . (See Figure 4.16, but add one electron.) Thus the structural changes are less pronounced than for corresponding iron(II) systems.<sup>110,111</sup> From the similarities in



geometries and differences in electronic structures between cobalt- substituted and native hemoglobins and their models, many insights have been gained about the factors that determine oxygen affinity as well as how cooperativity might, or might not, work at the molecular level.<sup>112,113</sup> The mechanism of cooperativity has also been probed by the substitution of other metallocporphyrins into the globin: for example, zinc porphyrins have been used for their excited triplet-state properties,<sup>114</sup> manganese porphyrins for their EPR activity,<sup>115</sup> and ruthenium porphyrins as a member of the iron triad.<sup>116</sup>

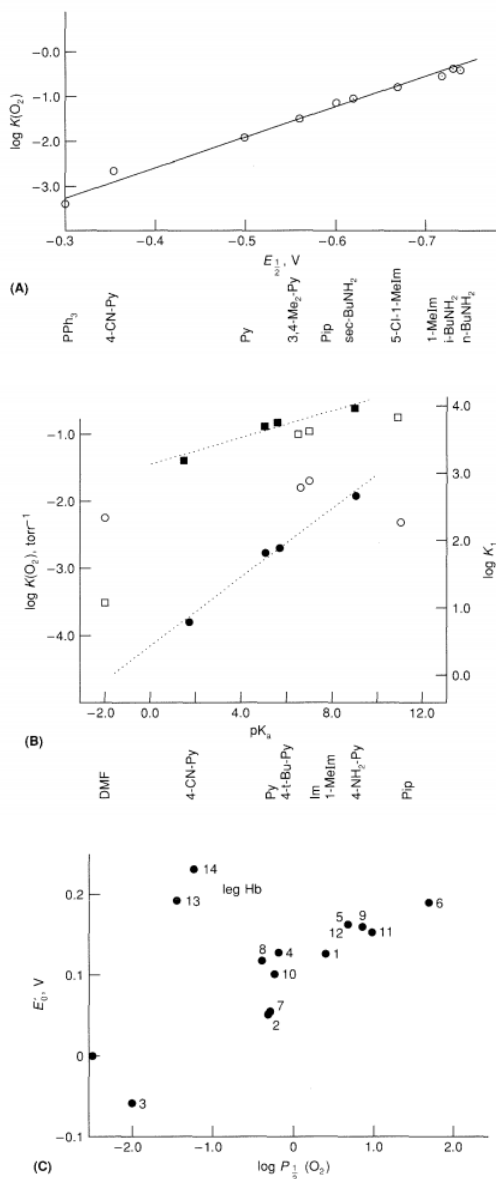


Figure 4.18 - Linear free-energy relationships: (A) Correlation of the  $\text{O}_2$  affinity at  $-21^\circ\text{C}$  of  $\text{Co}(\text{bzacen})\text{L}$  with the  $\text{CO}^{\text{III}} \rightleftharpoons \text{CO}^{\text{II}}$  cyclic voltammetric wave of  $\text{Co}(\text{bzacen})\text{L}_2$  species,<sup>104a</sup> (B) Correlation of ligand affinity with  $\text{pK}_a$ . Squares ( $\square$ ) pertain to the binding of  $\text{L}$  to  $\text{Co}(\text{PPIX})$  at  $23^\circ\text{C}$ . Circles ( $\circ$ ) pertain to the  $\text{O}_2$  affinity at  $-45^\circ\text{C}$  of  $\text{Co}(\text{PPIX})\text{L}$  species, Filled shapes pertain to substituted pyridines; the least-squares lines shown are calculated from these data only,<sup>104a</sup> (C) Correlation of  $E_0'$  (from cyclic voltammetry) with affinity for a miscellany of hemoglobins:<sup>108</sup> 1, *Aphysia limacina* Mb; 2, *Physeter macrocephalus* Mb; 3, *Candida mycoderma* Hb; 4, *Chironomus thummi* Hb; 5, *Hb<sub>M</sub>-Hyde Park*; 6, *Hb<sub>M</sub>-Iwate*; 7, *Hb  $\alpha$  chain*; 8, *Hb  $\beta$  chain*; 9, *Hb F*; 10, *Hb  $\gamma$  chain*; 11, *HbA*; 12, *Glycera dibranchiata*; 13, *legHb-a*; 14, *legHb-c*, Reproduced with permission from A. W. Addison and S. Burman, *Biochim. Biophys. Acta* **828** (1985), 362-368.

\* Because the O—O stretch may be coupled with other ligand modes,<sup>109</sup> its value should not be used to estimate superoxo character, although in a series of  $\mu$ -superoxo and  $\mu$ -peroxo complexes of carefully controlled stereochemistry, small changes in  $\nu(\text{O}—\text{O})$  have been correlated with the  $\text{pK}_a$  of the suite of ligands.<sup>66</sup>



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