Thermodynamics of Oxygen Binding in Natural and Synthetic Dioxygen Complexes†

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I. Introduction

A. Significance of Dioxygen Complexes

The reversible reactions of dioxygen (O_2)[1] with protein complexes containing iron(II) or copper(I) are of critical importance to advanced and primitive forms of animal life.[2] The proteins involved include hemoglobin[3,4] in mammals,[5] birds, fish, and insects,[2] myoglobin in a variety of vertebrates and invertebrates,[5,6] erthrocruorin in snails and earthworms,[2,7] hemerythrin[8] and chlorocruorin in marine worms,[2,9,10] and hemocyanin in mollusks and arthropods[11-13] (Table I). A similar role has also been suggested for hemovanadin, found in ascidians[14-16] in which a vanadium(II) complex combines with dioxygen. Because these proteins can bind, transport, store, and release dioxygen, respiration may occur at sites remote from the external atmosphere.[17] A method of dioxygen transport incorporating both respiratory and circulatory features is essential to the existence of large, compact, multicellular animals, since the low ratio of surface area to volume in these animals prevents simple diffusion from meeting the dioxygen demands of respiration.[18] The human lungs for example have a surface area which is 30–50 times greater than the external surface area of the body. The equilibria involved in the transport of dioxygen to the site of utilization in a typical mammal are shown in Figure 1. Naturally, the details of dioxygen binding and transport in these proteins are of great interest to biochemists and numerous reviews of these and related subjects are available.[2-15,20-33] The structures and properties of these proteins, which are also of interest to chemists who design and study metal complexes as models for dioxygen transport proteins, have been reported in detail.[34-38]

The irreversible reactions of dioxygen with metalloproteins and organic substrates are also critically important to biological systems. Table II gives some indication of the variety of metal-catalyzed reactions which dioxygen can undergo. Reactions involving the catalytic insertion of one or both atoms of dioxygen into an organic substrate are of obvious importance in the synthesis of metabolic products and intermediates. The enzymes involved normally contain heme or non-heme

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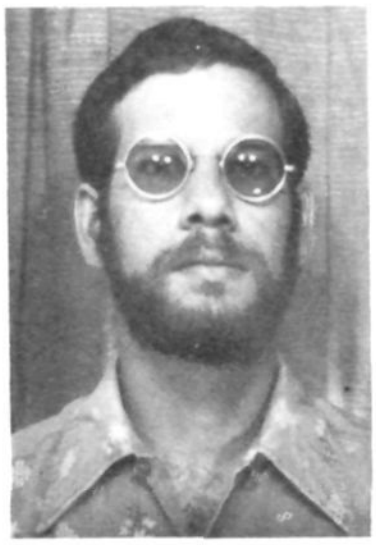


Eric C. Niederhoffer was born in New York City in 1957. He graduated from Stuyvesant High School (1975) and attended the University of Rochester where he obtained the Bachelor of Science degree in Chemistry (1979) and the Bachelor of Arts degree in History (1979). Senior research involved the thermodynamics of proton conformer equilibria under the direction of Dr. George McLendon. Doctoral studies were supervised by Dr. Arthur E. Martell at Texas A&M University (Ph.D. 1983). The dissertation research involved the autoxidation mechanisms of cobalt dioxygen complexes containing aromatic heterocyclic ligands. His research interests are concerned with the activation of small molecules by transition-metal complexes, inorganic photochemistry, and electron-transfer reactions. Presently he is studying the role of nickel in methanogenic bacteria as a postdoctoral fellow with Dr. W. H. Orme-Johnson at Massachusetts Institute of Technology.

James H. Timmons was born on November 3, 1954, in Waco, TX, was educated in Waco public schools, and attended Baylor University, from which he graduated in 1976, Magna Cum Laude, with a B.S. in Chemistry. He then entered the graduate program in chemistry at Texas A&M. In the course of his doctoral studies at Texas A&M, Dr. Timmons carried out potentiometric, calorimetric, and X-ray crystallographic studies of dioxygen complex formation and of macrocyclic complexes as models for copper proteins. After receiving his Ph.D. degree in 1980, he joined the University of Texas Medical School at Dallas, where he is completing studies toward the M.D. degree. Currently, he is planning his residency in diagnostic radiology. His long-range objectives involve the application of inorganic chemistry to medical research.

iron or copper; the reactions proceed through a dioxygen complex intermediate. Dioxygen also serves as an electron sink in the oxidation of a variety of small biomolecules including ascorbic acid (ascorbic acid oxidase), catechols (tyrosinase), and amino acids (amino acid oxidase).[39]

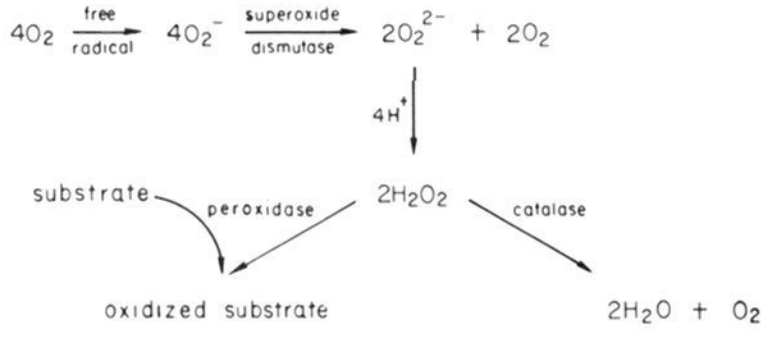
Superoxide dismutase, an enzyme containing copper with zinc, iron, or manganese, serves to protect organisms from the toxic effects of superoxide,[40-45] formed from dioxygen in the presence of free radicals. Superoxide dismutase forms dioxygen and peroxide by the cyclic process shown in eq 1 and 2. The reaction is

$$\mathrm{ECu(II)} + \mathrm{O_2^-} \rightarrow \mathrm{ECu(I)} + \mathrm{O_2} \qquad (1)$$

Arthur E. Martell, Distinguished Professor of Chemistry at Texas A&M since 1973, was also Head of the Chemistry Department there from 1966 to 1980. Formerly he was Professor of Chemistry and Chemistry Department Head or Chairman at Illinois Institute of Technology (1961–1966) and Clark University (1942–1961). Born in Natick, MA, October 18, 1916, he attended Worcester Polytechnic Institute, receiving the B.S. degree with high honors in 1938. After receiving the Ph.D. degree from New York University (University Heights) in 1941, he entered academic work as Instructor in Chemistry at WPI. At Clark he undertook research on metal chelate compounds and has remained active in that and related fields. He has authored, coauthored, or edited 15 books and 340 research papers on the equilibria, kinetics, and catalytic effects of metal chelate compounds.

$$\mathrm{ECu(I)} + \mathrm{O_2^-} + 2\mathrm{H^+} \rightarrow \mathrm{ECu(II)} + \mathrm{H_2O_2} \qquad (2)$$

driven by protonation of the peroxide ion (O_2^{2-}).[46] Whether the superoxide dismutase reactions involve a dioxygen complex intermediate is uncertain; the active site has not been completely characterized.[47] Superoxide can be generated by an outer-sphere process[48-51] and a metalloporphyrin lacking a free coordination site so that a dioxygen complex is not an obligatory intermediate in superoxide formation. Peroxide is toxic and must also be removed. Peroxide is either activated for subsequent insertion reactions by peroxidase, a heme protein, or disproportionated to water and dioxygen by catalase, another heme protein. These reactions involve dioxygen complex intermediates. While superoxide dismutase is found in all organisms, catalase is absent in strict anaerobes (e.g., clostridum).[52] The overall dioxygen protection mechanism is summarized in eq 3.



(3)

Both synthetic and natural complexes which reversibly bind dioxygen are termed *oxygen carriers*.[53] In addition to their significance as models[54] of the natural oxygen carriers, synthetic dioxygen complexes have potential applications in dioxygen separation and storage,[55] industrial processes,[56,57] and catalysis.[58] Until recently, the industrial interest in dioxygen complexes centered around modeling of industrially important reactions of dioxygen, including the contact process for manufacturing sulfuric acid and the Ostwald process for the synthesis of nitric acid.[56] Recently, however, manganese dioxygen complexes have been suggested for use in separating dioxygen from air by a pressure swing

TABLE I. Protein Oxygen Carriers[a]

protein	metal	source	location	$P_{1/2}$,[b] torr
hemoglobin (Hb)	Fe (heme)	mammals	corpuscles	27 (man)[c]
		birds	corpuscles	58 (chicken)[c]
		fish	corpuscles	18 (salmon)[c]
		insects		~3 (*Chironomus thumni thumni*)[d]
myoglobin (Mb)	Fe (heme)	mammals	muscle	1 (horse heart)[e]
		other vertebrates	muscle	
		some invertebrates	muscle	
erythrocruorin (Ery)	Fe (heme)	snail	plasma	3 (planorbis)[c]
		lugworm	plasma	2 (arenicola)[c]
		earthworm	plasma	8 (lumbricus)[c]
chlorocruorin (Chl)	Fe (heme)	marine worms	plasma	27 (spirographis)[c]
hemerythrin (Her)	Fe (non-heme)	marine worms	corpuscles	3 (golfingia)[c]
hemocyanin (Hcy)	Cu	mollusks	plasma	5 (octopus)[c]
		arthropods	plasma	14 (lobster)[c]
hemovanadin[f] (Hv)	V	ascidians	corpuscles	2 (sea squirt)[c]

[a] Adapted from ref 2. [b] Pressure at which the protein is half-saturated with dioxygen. [c] Values obtained under physiological conditions. [d] Values range from 1.79 to 4.00 and from 1.09 to 5.35 for the two Hb components at 37 °C. See ref 451. [e] Value for stripped protein. See ref 510. [f] The respiratory function of this protein is disputed. See ref 16.

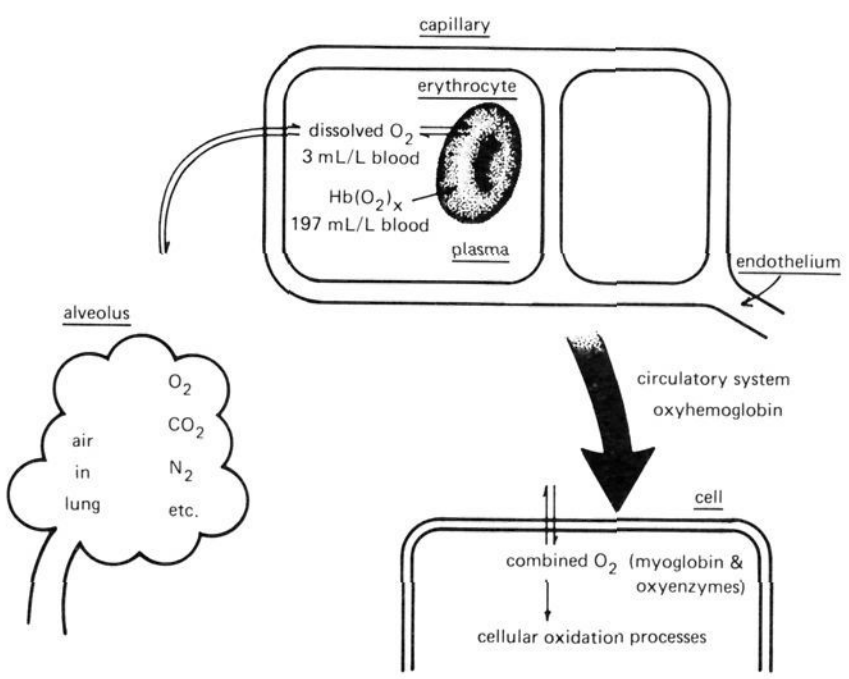


Figure 1. Dioxygen transport process in a typical mammalian system (magnified section). Adapted from ref 17 and 18.

absorption process and for scavenging minute traces of dioxygen from inert atmospheres.[57] Patent applications[59] have been filed in the United Kingdom for these latter uses. Patents have also been filed for the use of polymer-bound cobalt salicylaldimine complexes[60] and cobalt and iron porphyrin complexes[61] as dioxygen sorbents.

Interest in the catalytic aspects of dioxygen complexes has intensified in recent years.[58,62] Simple cobalt complexes with 1,6-bis(2-hydroxyphenyl)-2,5-diaza-1,5-hexadiene (SALEN) or polyamines and related ligands have been employed successfully as catalysts.[63–65] These compounds promote reactions similar or identical with those promoted in biological systems[66,67] by dioxygenases such as pyrocatechase[68] and monooxygenases (mixed-function oxidases) such as cytochrome P_{450}.[69–71] They act in some cases in a catalytic fashion and in other cases in a stoichiometric fashion. Some oxygenases and oxygenase model systems, along with the reactions which they promote, are listed in Table III. "Vaska-type" dioxygen complexes exhibit a number of potentially valuable catalytic and stoichiometric reactions which are not, in general, directly analogous to biochemical systems.[56,58] Some of these are illustrated in Table IV. The activation of dioxygen

TABLE II. Metal-Catalyzed Reactions of Molecular Oxygen[a]

Insertion of Dioxygen
- A. with cleavage of O-O bond
  - 1. total insertion
    - a. dioxygenases (e.g., pyrocatechase)
    - b. reaction of $CH_3COC_6H_5$ with O_2 to form $HOOCC_6H_5$ (catalyzed by Mn(III))
  - 2. peroxide reactions
    - a. Fenton's reagent
    - b. model peroxidase systems
    - c. enzyme systems
  - 3. single oxygen insertion
    - a. Udenfriend's system
    - b. free-radical reactions of O_2
    - c. monooxygenases
- B. without cleavage of O-O bond
  - 1. formation of organic peroxides $RR + O_2 \rightarrow ROOR$
  - 2. reactions of organometallic compounds $MR + O_2 \rightarrow MOOR$

Reactions Not Involving Dioxygen Insertion
- A. reduction of O_2 to H_2O_2
  - 1. oxidation by oxygen carriers
  - 2. metal ion catalyzed oxidation of ascorbic acid, catechols, etc.
  - 3. enzymatic reactions catalyzed by uricase, amine oxidases, oxalate reductase, etc.
- B. stepwise reduction of O_2 to H_2O
  - 1. reduction by oxidases (e.g., tyrosinase, laccase, polyphenol oxidases, etc.)
  - 2. free-radical coupling reactions
  - 3. enzymic coupling reactions

Disproportionation of H_2O_2
- A. catalase enzymes
- B. catalase model systems

Disproportionation of O_2^-
- A. superoxide dismutase enzymes
- B. superoxide dismutase model systems

[a] Adapted from p 655 of ref 80.

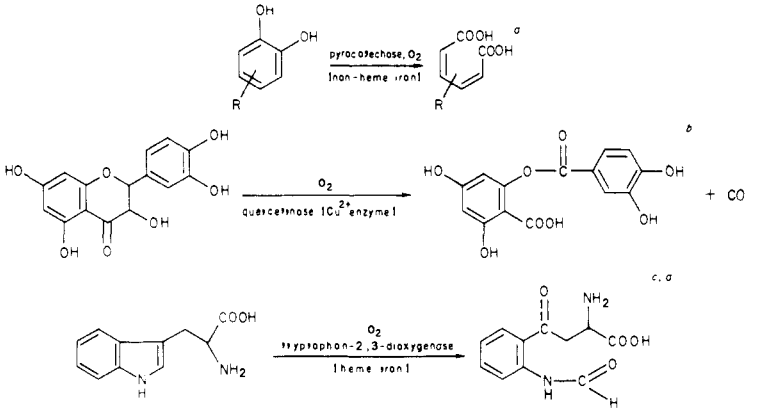
for subsequent reaction has been discussed in a number of reviews.[63,72,73]

Recent papers describe catalysis of the electroreduction of dioxygen to water[74] or peroxide[75–77] by complexes which bind dioxygen. These studies have important implications for fuel-cell and air-battery technologies. One complex, a bifacial porphyrin with two bound cobalt(III) ions (Figure 2), reduces dioxygen to water at a potential of 0.72 V (vs. NHE) with less than 1% production of H_2O_2 when adsorbed on a graphite electrode.[74] The suggested mechanism is illustrated in Figure 2. Apparently the distance between the metal

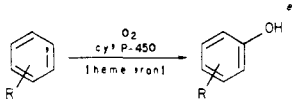
TABLE III. Reactions Catalyzed by Oxygenases and Oxygenase Model Systems

Enzyme Systems

dioxygenases

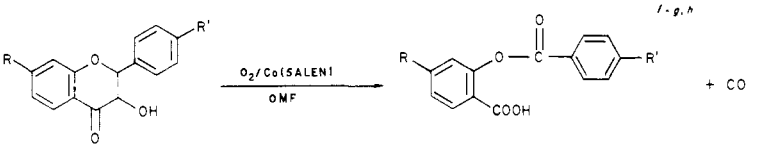


monooxygenases

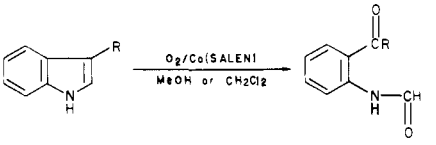


Model Systems

dioxygenase models

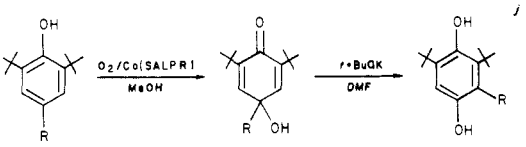


R = R' = H, OH, OMe



R = Me, $CH_2CH_2COOCH_3$, $CH_2CH_2NHCOCH_3$

monoxygenase models



R = *t*-Bu, *i*-Pr, Et, Me

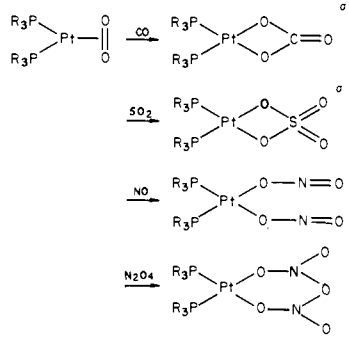
[a] Nozaki, M. In "Molecular Mechanism of Oxygen Activation"; Hayaishi, O., Ed.; Academic Press New York, 1974, p 135. [b] Westlake, D. W. S.; Talbot, G.; Blakely, E. R.; Simpson, F. J. *Can. J. Microbiol.* 1959, *5*, 621. Hattori, S.; Noguchi, I. *Nature (London)* 1959, *184*, 1145. Oka, T.; Krishnamurty, H. G.; Simpson, F. J. *Can. J. Microbiol.* 1972, *18*, 493. [c] Feigelson, P.; Brady, F. O. In footnote *a*, p 87. Ishimura, Y.; Nozaki, M.; Hayaishi, O.; Nakamura, T.; Yamazaki, I. *J. Biol. Chem.* 1970, *245*, 3539. [d] Related reactions of indoleamine-2,3-dioxygenase are covered in a paper by Hirata et al.: Hirata, F.; Hayaishi, O.; Tokuyama, T.; Senah, S. *J. Biol. Chem.* 1974, *249*, 1311. Hirata, F.; Hayaishi, O. *J. Biol. Chem.* 1975, *250*, 5960. [e] Daly, J.; Guroff, G.; Jerina, D.; Udenfriend, S.; Witkop, B. *Adv. Chem. Ser.* 1973, *No. 77*, 279. Hamilton, G. A. In footnote *a*, p 405. [f] Nishinaga, A.; Tojo, T.; Matsuura, T. *J. Chem. Soc., Chem. Commun.* 1974, 896. [g] Only occurs in the presence of a metal dioxygen complex. [h] CO is converted to CO_2 under the reaction conditions employed. [i] Reference 65. [j] Nishinaga, A.; Watanabe, K.; Matsuura, T. *Tetrahedron Lett.* 1974, 1291. Nishinaga, A.; Itahara, T.; Matsuura, T.; Berger, S.; Henes, G.; Rieker, A. *Chem. Ber.* 1976, *109*, 1530.

centers as controlled by the bifacial porphyrin is important since *trans*-$[Co(TACTD)(OH_2)_2]^{3+}$ [76] reduces dioxygen only to hydrogen peroxide. A series of iron porphyrin complexes[77] has been synthesized which will catalytically reduce dioxygen to water, but in this case the reduction occurs with intermediate formation of peroxide. A variety of copper(I) complexes has been reported to catalyze the reduction of dioxygen to water and the oxidation of primary and secondary alcohols to aldehydes and ketones, respectively, in analogy to Cu(I)-containing oxidases.[78]

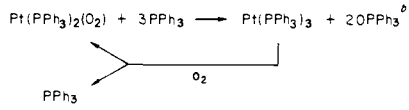
Dioxygen complexes are of academic interest because

TABLE IV. Some Stoichiometric and Catalytic Reactions of "Vaska" Complexes

stoichiometric



catalytic



[a] Reference 141. [b] Birk, J. P.; Halpern, J.; Pickard, A. L. *J. Am. Chem. Soc.* 1968, *90*, 4491. Halpern, J.; Pickard, A. L. *Inorg. Chem.* 1970, *9*, 2798.

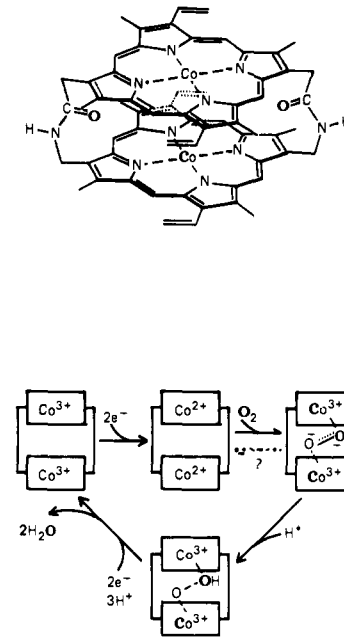


Figure 2. (Top) Bifacial porphyrin complex which catalyzes electroreduction of dioxygen to water. (Bottom) Proposed mechanism of electrocatalysis by the bifacial porphyrin indicated above.

they exhibit a wide range of stabilities and reactivities which vary predictably with changes in the ligands employed. They also display interesting structural and electronic properties.[79] In addition, they play a major part in the more general field of metal-catalyzed reactions of molecular oxygen[80,81] (Tables II, III, IV).

There are many scholarly reviews of the formation and properties of synthetic dioxygen complexes,[34-38,56,80-107] but a thorough review of the thermodynamic properties of these compounds has not been previously available even though hundreds of thermodynamic values for oxygen carriers have been determined and a theoretical background for their interpretation exists. The present review provides a comprehensive classified analysis of the thermodynamics of dioxygen complex formation and suggestions for interpretative correlations of the energetics of dioxygen binding with chemical properties of the complexes formed. This review should prove especially valuable in the future development of catalytic and model systems, both of which are highly dependent on thermodynamic variables, and as a detailed supplement to more general reviews of properties of dioxygen complexes.

Although the reaction of dioxygen with a metal complex is termed oxygenation, not all products of such reactions are dioxygen complexes. Complexes in which dioxygen appears (in any oxidation state) are termed dioxygen complexes only when reversibility of the oxygenation reaction is demonstrated. This reversibility may be established in a number of ways. In the simplest case the formation of a dioxygen complex from dioxygen and a metal chelate may be reversed by heating and/or reducing the pressure of the system. For very stable dioxygen complexes lowering the pH of the aqueous solution will result in the dissociation of the bound dioxygen. Some situations are more complicated and reversibility is difficult to demonstrate. If in these cases the intermediate dioxyen complex may be formed from dioxygen *and* if dioxygen can be recovered, at least in part, by a change in conditions, the reversibility requirement will be considered satisfied.

B. Scope

In this review, a complete tabulation of the stability constants of synthetic dioxygen complexes reported in the literature is provided (Appendix I), along with other thermodynamic constants (e.g., $\Delta H°$, $\Delta S°$, etc.) that are currently available. Emphasis is placed on interpretation of thermodynamic data in terms of metal–ligand bonding and reactivities of the dioxygen complexes. Relationships between thermodynamic constants (e.g., oxidation potentials of cobalt(II) complexes and the stabilities of the corresponding dioxygen complexes) are described. Special consideration is given to the prediction of dioxygen affinities of metal complexes from their physical properties. Experimental methods used to determine the thermodynamic properties are given critical consideration.

Because of the considerable variety and extent of thermodynamic studies of dioxygen transport proteins, no attempt has been made to include every paper in this area. An extensive, selective tabulation of thermodynamic constants of natural oxygen carriers drawn mainly from the recent literature has been included (Appendix II). It is hoped that this treatment will provide a convenient bibliographic resource for those interested in biological dioxygen transport and thereby aid in the development of new model systems. The discussion of biological oxygen carriers will emphasize thermodynamic aspects of dioxygen binding by these systems and comparisons with model systems, although other considerations will also be included. Questions concerning the roles of the various portions of oxygen transport proteins will be considered. Comparisons between dioxygen transport proteins and synthetic oxygen carriers will also be used to explore some of the properties of the latter compounds. Some discussion of dioxygen complexes as intermediates in metal-cata-

TABLE V. Properties of Dioxygen in Various Oxidation States[a]

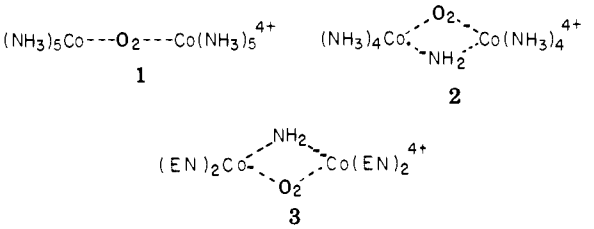
species	compd	O-O distance, Å	ν(O-O), cm^{-1}	bond order	bond energy, kcal/mol
O_2^+	O_2AsF_6	1.123[b]	1858[c]	2.5	149.4[d]
$O_2(^3\Sigma_g^-)$	O_2	1.207[b]	1554.7[d]	2	117.2
$O_2(^1\Delta_g)$	O_2	1.216[e]	1483.5[f]	2	94.7[g]
O_2^-	KO_2	1.33[h]	1145[i]	1.5	
	LiO_2		1097[j]	1.5	
O_2^{2-}	H_2O_2	1.49[k]		1	35[l]
	Na_2O_2	1.49[m]	842[n]	1	48.8[g]
	Li_2O_2		802[j]	1	

[a] Adapted from tables in ref 56 and 102. [b] Abrahams, J. C. *Q. Rev., Chem. Soc.* 1956, *10*, 407. [c] Shamir, J.; Beneboym, J.; Classen, H. H. *J. Am. Chem. Soc.*, 1968, *90*, 6223. [d] Reference 258. [e] Kasha, M.; Khan, U. A. *Ann. N.Y. Acad. Sci.* 1970, *171*, 5. [f] Reference 257. [g] Reference 102. [h] Halverson, F. *Phys. Chem. Solids* 1962, *23*, 207. [i] Reference 256. [j] Reference 96. [k] Cotton, F. A.; Wilkinson, G. "Advanced Inorganic Chemistry" 4th ed.; Wiley-Interscience: New York, 1980; p 499. [l] Taube, H. *J. Gen. Physiol.* 1964, *49*, 29. [m] Fener, S. N.; Hudson, R. L. *J. Chem. Phys.* 1962, *36*, 2676. [n] Evans, J. C. *J. Chem. Soc. D* 1969, 682.

lyzed oxidations of organic substances, including biological oxidations, will be included. The emphasis will again be on interpretation of thermodynamic data and comparison of biological systems with model systems.

C. Historical Background

The fact that aqueous ammonia solutions of cobalt(II) salts turn brown when exposed to air was discovered over a century ago.[108,110] Alfred Werner was the first chemist to characterize dioxygen complexes.[110,111] He correctly formulated compound 1 as a cobalt(III) dinuclear complex with a peroxide bridge. Unfortu-



nately, his assumption that complexes such as 2 and 3 also contained peroxide led him to formulate them as mixed Co(III)/Co(IV) complexes. Compounds 2 and 3 were later shown to be superoxo complexes.[112,113]

The reversibility of dioxygen adduct formation was not demonstrated until 1938, when Tsumaki[114] showed that the color change observed[115] upon exposing Co^{II}(SALEN) to air was due to reversible oxygenation. Calvin et al. and Diehl et al. later studied extensively the oxygen carrier properties of Co(II) complexes with SALEN-type ligands.[116-122] These studies were directed toward the development of a lightweight system to store dioxygen for military applications. The results are disappointing because the dioxygen carrying ability of the chelates deteriorated over a relatively short number of oxygenation/deoxygenation cycles. Co^{II}(SALEN), for example, deteriorates to 70% of its original activity after only 300 cycles.[118] Studies on the oxygenation/deoxygenation of [1,6-bis(2-hydroxy-3-fluorophenyl)-2,5-diaza-1,5-hexadiene]cobalt(II) (Fluomine) by a combination of gas chromatographic and thermogravimetric methods indicate that deterioration is the result of irreversible oxidation of the ligand by dioxygen, resulting ultimately in the formation of CO_2 and H_2O.[123] A system for military aviation has been developed recently,[55] but it has not yet been employed.

At approximately the same time that Calvin was performing his studies, Hearon et al. reported dioxygen adduct formation by cobaltous bis(histidine) in solution.[124-127] Although this work received little attention at the time, it demonstrated that reversible oxygenation is a general rather than an isolated phenomenon. The chemistry of oxygen carriers was first reviewed in 1952.[82] Aside from this, however, the field received little attention until the sixties.[83-86] Renewed interest resulted mainly from attempts to model hemoglobin,[102] a compound which has been termed "an inspiration for research in coordination chemistry".[128]

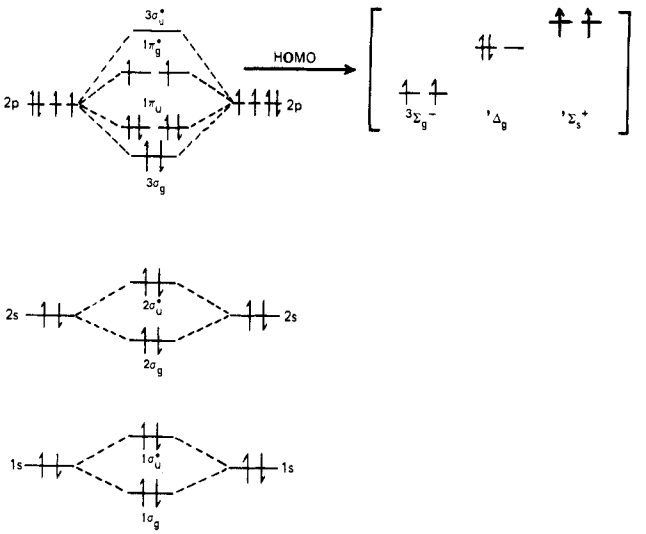


Figure 3. Molecular orbital diagram for dioxygen showing electron configurations of the highest occupied molecular orbitals (HOMO).

D. Dioxygen

Dioxygen is normally in a triplet state ($^3\Sigma_g^-$) having unpaired electrons as illustrated in Figure 3. The first excited state, a singlet ($^1\Delta_g$), is 22.5 kcal/mol higher in energy.[102,129] Another singlet excited state ($^1\Sigma_g^+$) lies 37.5 kcal/mol above the ground state.[102,129] This second singlet state has a short lifetime (10^{-12} s) in solution, rapidly relaxing to the longer lived (10^{-3}–10^{-6} s) first excited state through a spin-allowed transition.[130] Since electrons must be added to antibonding orbitals, reduction of dioxygen results in longer, weaker O–O bonds. Similarly, oxidation of dioxygen removes an electron from an antibonding orbital. The O–O bond is thus strengthened and shortened. These arguments

TABLE VI. Biologically Significant Reduction Potentials of Dioxygen Species

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$$

$$E^{\circ\prime} = 0.79 \text{ V vs. NHE}^a \quad \text{pH } 7.4,\ 25\ ^\circ\text{C}$$

$$O_2 + H^+ + e^- \rightarrow HO_2\cdot$$

$$E^\circ = -0.32 \text{ V vs. NHE}^b$$

$$HO_2\cdot + H^+ + e^- \rightarrow H_2O_2$$

$$E^\circ = 1.68 \text{ V vs. NHE}^b$$

[a] Reference 131. [b] George, P. In "Oxidases and Related Redox Systems"; University Park Press: Baltimore, MD, 1973; p 1.

are sufficient to explain the bond distances and IR frequencies for the various oxidation states of dioxygen, as given in Table V.

The chemical reaction of dioxygen which is of major importance for biological systems and for oxygenation reactions is reduction. The free energy change for four-electron reduction of dioxygen (to two water molecules) is negative by 316 kJ/mol at pH 7 (eq 4).[101,131] The potential is quite attractive for energy

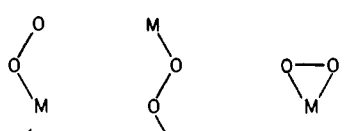
$$O_2 + 4H^+ + 4e^- \rightleftharpoons 2H_2O$$

$$E^{\circ\prime} = +0.815 \text{ V (vs. NHE)} \qquad (4)$$

storage. Such a reduction process does not occur in one step but rather through a series of steps involving successive one-electron transfers.[101,132] Mechanistic limitations severely restrict the usefulness of the reduction. The most common pathway for dioxygen reduction is one-electron transfer followed by disproportionation to form OH^- under basic conditions or H_2O_2 under acidic conditions.[133,134] The effective potential (Table VI) is pH independent and the one-electron reduction is endothermic by 128 kJ/mol.[101] The reverse of eq 4 is also of major importance since it represents the overall oxidation process which occurs in photosynthesis. As before, however, the reaction proceeds by one- and two-electron steps rather than by a single four-electron oxidation.[101]

1. Dioxygen as a Ligand

Since the reaction between dioxygen and metal ions is a redox process, it is most easily discussed in terms of the electron-donor properties of the metal ion. One-electron reductants react with dioxygen to form complexes having molar dioxygen to metal ratios of 1:1[135,145] or 1:2,[146-152] with binding as shown in 4 and 5, respectively, for these two stoichiometries. In this



4 5 6

review, complexes of type 4 are formally considered superoxide complexes of one-electron-oxidized metal ions,[153] while those of type 5 are analogously viewed as μ-peroxo complexes.[56] Actually, electron transfer to dioxygen is generally incomplete for reversible oxygen carriers;[154,155] the metal ion has properties intermediate

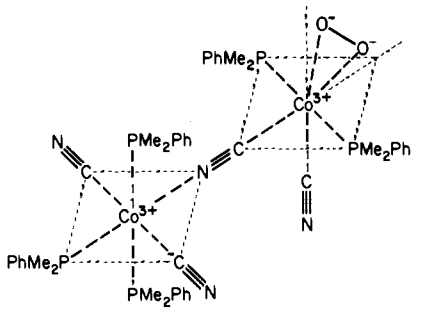
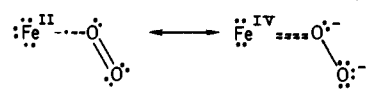


Figure 4. Representation of the coordination sphere $[(Co_2)(CN)_4(PMe_2Ph)_5(O_2)]$. Adapted from ref 156.

between those of the higher and lower oxidation states.[102,153] Two-electron donors form complexes of type 6[56] through what is generally considered an oxidative addition type reaction. Although the oxidation state is even more ambiguous for this type of complex than for the one-electron donor complexes,[56] type 6 is normally viewed as a peroxide bound to a metal ion which has undergone a two-electron oxidation. Under certain conditions, two one-electron-donor metal centers can interact with dioxygen as if they were a single two-electron donor,[156] such that type 6 bonding results. This type of oxygenation is demonstrated by the formation of $[Co_2(CN)_4(PMe_2Ph)_5(O_2)]$ (Figure 4). Compounds containing S_2 and which are analogous to the dioxygen complexes with structures 5[157,158] and 6[159-168] have been prepared and characterized. Both types have also been structurally characterized.[157,162,164,166]

2. Oxidation States in Dioxygen Complexes

Not all authors agree that complexes of type 4 should be described as superoxo complexes. Indeed, the arguments in this area have been so intense that they have been labeled arguments of "religious persuasion" by Reed.[100] In order to support the position taken here, it is necessary to review the arguments supporting the $Fe^{II}O_2(0)$ and the $Fe^{(III)}O_2(-1,0)$ descriptions. Pauling and Coryell first reported the diamagnetism of oxyhemoglobin (HbO_2) in 1936.[169] Pauling assumed that there is an even number of electrons about dioxygen. He therefore predicted bent, end-on binding of dioxygen to hemoglobin[169,170] as described by the two resonance structures 7 and 8. Griffith[171] proposed a



7 8

different model in which dioxygen contributes electron density from its π-bonding orbital into an Fe(II) d^2sp^3 orbital. Fe(II) could then back-bond to the dioxygen π^* orbital (Figure 5). This model is analogous to the binding of ethylene to platinum in Zeise's salt[172] and the bonding in related organometallic compounds as described by Chatt and Duncanson.[173] The resulting compound would have dioxygen bound side-on as shown in 6. Such a structure would be unique for iron complexes and is no longer given much consideration.

The Griffith model was later extended to Vaska's complex[174] ($[IrCl(CO)(P(C_6H_5)_3)_2]$) and similar complexes,[175,176] where it has proved to be quite adequate. However, it is no longer considered to be a valid model

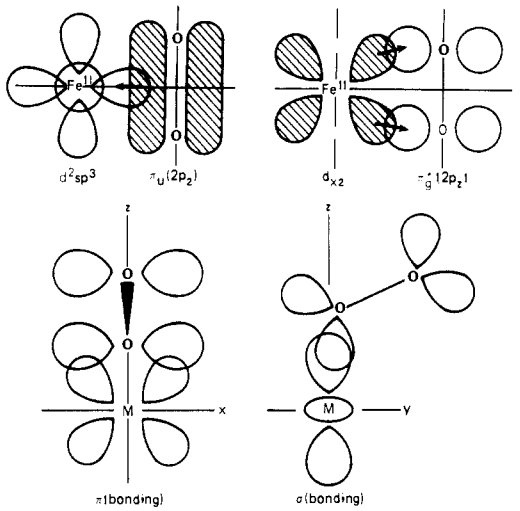
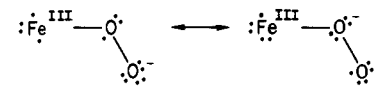


Figure 5. (Top) Griffith bonding mode for dioxygen complexes. (Bottom) Reed/Cheung bonding mode for dioxygen complexes. Adapted from ref 153.

for hemoglobin.[100] The first convincing argument against the occurrence of Griffith bonding in HbO_2 was the crystal structure[177,178] of an iron "picket fence" compound which is remarkably similar to hemoglobin. This and similar compounds exhibit bent, end-on dioxygen binding (type 4).[177-179] The remarkable similarity between the "Mössbauer" data for HbO_2[180,181] and the "picket fence" compound[182-184] leaves little doubt that the bonding mode is identical in the two species.[100] It should also be noted that the IR stretching frequency (ν_{O-O}) for human oxyhemoglobin A (HbA) reconstituted from the apoprotein and ferrous deuteroporphyrin differs from that for a protein reconstituted from cobaltous deuteroporphyrin and apoprotein by only 1 cm^{-1}.[185] This is important since strong evidence exists for type 4 bonding geometry in dioxygen adducts of Co(II).[98] In fact of the Co(II) dioxygen complexes which have been structurally characterized by single-crystal X-ray diffraction,[112,113,186-224] all but one[156] have either the 4 or 5 bonding geometry. The Griffith structure is seen only in dioxygen complexes formed from cobalt(I) complexes containing very basic arsine or phosphine ligands.[225,226]

An early study of the structure of sperm whale oxymyoglobin,[227] while suggestive of Pauling bonding, was inconclusive. Structural studies of oxy-[228] and deoxyhemoglobin[229-231] by Perutz et al. were directed toward defining the factors responsible for cooperativity in dioxygen binding. Specific quaternary structural changes between low-affinity and high-affinity forms of hemoglobin were elucidated in the studies. This allowed theories for the mechanisms of control of the quaternary structure changes to be proposed by Perutz et al.[232-234] and by the others.[235,236] However, the geometry of the bound dioxygen was not investigated by protein crystal structures until 1978. In oxyerythrocruorin[7,237] dioxygen is bound end-on and is bent with an (estimated) Fe–O–O angle of 170°. The oxygen not directly bound to iron is hydrogen bonded to water. Recent crystallographic studies on oxymyoglobin[238,239] and oxyhemoglobin[240] have confirmed the bent, end-on bonding mode. The Fe–O–O angles at the present level of refinement are 115° and 156°, respectively. A neutral diffraction study on oxymyoglobin[241] reveals the presence of hydrogen bonding between the distal histidine (HIS-βE7) and the noncoordinated end of the dioxygen ligand. In work by Shaanan[240] the distal histidine is shown to be within close enough proximity to the dioxygen to form strong hydrogen bonds only in the α subunits. Hydrogen bonding between the distal histidine and the dioxygen in the β subunits would be weaker since the contact distance is increased. Recent resonance Raman work by Kitagawa et al.[242] supports the presence of hydrogen bonding in mixed-metal iron–cobalt hybrid hemoglobins and myoglobins. In these systems the $\bar{\nu}(O_2)$ but not $\bar{\nu}(Co-O)$ is shifted when the solvent changes from H_2O to D_2O. Although the Co(III)–O–O and O–O bonds would be expected to have coupled vibrations, the hydrogen bond which is approximately perpendicular to the O–O bond does not generate a measurable shift in $\bar{\nu}(Co-O)$.

A third model for dioxygen binding in HbO_2 was proposed by Weiss[243] and extended by others.[244] This model assumes an odd number of electrons on dioxygen with coupling between the unpaired electron on Fe(III) and that on dioxygen. This model is represented by the resonance forms **9** and **10**. Yet another model suggested by Tovrog and Drago[245a,b] and Veillard and coworkers[245c] has $^1\Delta_g$ dioxygen bound to Fe(II) (the model actually used was a Co(II) model, but it is readily extended to HbO_2). The latter model has been criticized by Basolo et al.[102] Their calculations reveal that the Fe–O bond energy for an Fe(II)–O_2 ($^1\Delta_g$) would be 38 kcal/mol, a value which they consider unrealistic. Drago[246] has rejoined that the singlet oxygen formulation was as useful as the Co(III)–O_2^- formulation, given the data available at the time (mainly EPR spectral data). Data obtained since that time on the ^{17}O hyperfine coupling[154] have resulted in modification of the previous interpretations of both Drago[245] and others[247,248] because they demonstrate that the hyperfine coupling does not arise from delocalization of the unpaired electron on cobalt. The unpaired electron apparently resides on the dioxygen regardless of the extent of electron transfer into oxygen, which can vary from 0.1 to 0.8 of an electron.[154,249] Indirect as well as direct hyperfine couplings are required to explain the observed cobalt hyperfine structures.[250,251]



9 **10**

Reed and Cheung[153] have suggested that a simple $M^{III}(O_2^-)$ formulation is both justified and chemically reasonable. They see the entire debate as a "misunderstanding between experimentors who sought to impart a measure of the real electron density distribution and those who sought to represent chemically reasonable and useful formal oxidation states."[153] The $M^{III}(O_2^-)$ formulation can, in their view, rationalize the observed spin pairing and geometrical features of the dioxygen complexes if the bonding scheme illustrated in Figure 5b is employed. It also provides the most reasonable explanation of the spectral properties for these complexes. The infrared stretching frequencies of mononuclear coordinated dioxygen[181,185,252-255] resemble those of superoxide[256] or fall between those of superoxide and those of singlet[257] and triplet[258] molec-

ular oxygen. Both the ^{57}Fe Mössbauer[259] and Raman[260] spectra of HbO_2 are characteristic of Fe(III). The optical spectra of HbO_2 and alkaline methemoglobin (MetHb) show striking similarities.[177,178,261] Furthermore, HbO_2 is reported to be paramagnetic at low temperature,[282] although this claim is disputed.[283] Recent LCAO-MO-SCF-Cl calculations support the diamagnetic ground state for hemoglobin but reveal a very low-lying paramagnetic triplet state ~150 cm^{-1} above it.[264] Superoxide can be generated from HbO_2 by interaction with various anions;[265] flash photolysis of oxymyoglobin (MbO_2) with low-intensity (38 J) white light also gives superoxide anions and metmyoglobin (MetMb).[266] The only major disadvantage of the $Fe^{III}(O_2^-)$ formalism is that it fails to predict the actual electron distribution.[153] Therefore, this formalism is suggested as the most *useful* formalism for coordination chemists.[267] The assignment of a +3 oxidation state for iron and a -1 oxidation state for dioxygen is reasonable if Weiss' model[177,178] is employed. For purposes of charge distribution in a M-L complex the electron pair represented by a—is counted on L. Where the extent of electron transfer must be indicated, fractional oxidation states have been suggested.[153,167] Another reasonable interpretation is to visualize the III and -I oxidation states, partially modified by varying degrees of covalent character in the metal-dioxygen coordinate bond.

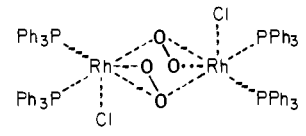
To appreciate the logic behind this position, one need only consider the definition of oxidation state.[267] The oxidation state is the electric charge which an atom in a molecule would have if the bonding were entirely ionic. Thus, an oxidation state is a formal device and should not be expected to predict the extent of electron transfer. Since the $M^{III}O_2(-I,0)$ formulation is also the formulation which gives the most accurate impression of the *chemical* nature of the bent, end-on dioxygen complexes, it should be adopted whenever a detailed molecular orbital discussion of the bonding is unwarranted. The more detailed bonding analyses have been performed by extended Huckel, ab initio Hartree-Fock, Xα multiple scattering, and extended Pariser-Parr-Pople methods[268] and more recently by a modified Fenske-Hall approach.[269] In these theoretical analyses the concept of oxidation state has little significance, especially where configurational interaction is employed.[269,270]

It should be noted that Drago[246] does not agree with the assignment of an oxidation state of +3 to Fe, Cr, or Mn but rather maintains that all of these must be in the +4 oxidation state. This position, however, has received no support from other investigators. Drago further argues that formulations such as $Fe^{III}(O_2^-)$ and $Co^{III}(O_2^-)$ are confusing, since they seem to imply an actual uninegative charge on dioxygen. This is a reasonable objection, and use of the formulation $M^{III}O_2(-I,0)$ is therefore advisable to avoid confusion.

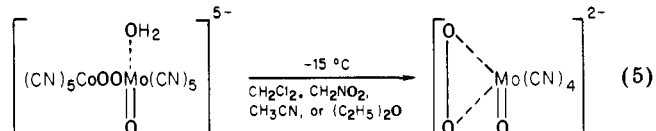
E. Metal Ions That Form Dioxygen Complexes

Table VII shows the metal ions that form dioxygen complexes either reversibly or irreversibly.[271-311] Most of these metal ions form complexes simply by reaction with either gaseous[57,312-314] or dissolved[35,315,316] dioxygen. A few complexes may be formed only by reaction with superoxide[317] or peroxide.[318,319] Normally, the dinuclear superoxo complexes may only be obtained by oxidation of the corresponding dinuclear peroxo complexes.[320-327] Specifically excluded from detailed discussion in this review are dioxygen complexes formed by cryochemical or matrix isolation techniques.[328]

Included in Table VII are dioxygen complexes which do not readily fit the normal classifications. A rhodium complex, **11**, exists which is a dimeric 1:1 ($M:O_2$) complex.[329-331] A heterobimetallic dioxygen complex, **12**,



11



12 **13**

with a peroxide ligand has also been prepared.[332,333] Upon standing in organic solvents at -15 °C, this complex rearranges to yield a peroxo complex of molybdenum, **13**.[332]

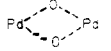
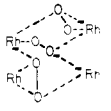
1. Stoichiometry and Coordinate Bonding in Dioxygen Complex Formation

Cobalt(II) complexes normally form 2:1, μ-peroxo-bridged complexes in aqueous solution.[83,84,90,334-346] Whenever the chelating agent has an insufficient number of coordinating groups or is present in insufficient concentration to completely saturate the coordination sites available on the cobalt ion, a second bridge may form.[347-352] The second bridge may be a μ-hydroxo-,[347-352,195] a μ-amido,[198] or another μ-type bridge.[203,353] When only one coordination site is available on each cobalt, formation of the second bridge is precluded. Several examples have been reported in which a monobridged complex is formed at low pH and a μ-peroxo-μ-hydroxo dibridged complex is formed at higher pH.[354-356] This supports previous arguments that the formation of a μ-peroxo bridge generally precedes μ-hydroxo bridge formation.[98] A μ-peroxo bridge may be formed intramolecularly[357] if a ligand capable of binding two metal ions simultaneously[358-360] with favorable geometry is employed.

Formation of μ-peroxo-bridged complexes of cobalt is preceded by formation of a 1:1 (cobalt:dioxygen), presumably superoxo, complex. This was first indicated by kinetic studies of the oxygenation of Co(TRIEN)$(H_2O)_2^{2+}$ [361,362] and was later confirmed by kinetic studies on Co(TETREN)$(H_2O)^{2+}$.[363] Kinetic studies also indicate that dissociation of the dibridged complexes is pH dependent, suggesting protonation of the hydroxo bridge prior to dissociation into the mononuclear metal chelates.[364,365] The proposed mechanism did not consider the formation of protonated metal chelate species which would also give a pH dependence to the dissociation of the dibridged dioxygen complexes.

It has been possible to limit the oxygenation reaction to 1:1 complex formation by using low dielectric con-

TABLE VII. Some Metal Ions That Form Dioxygen Complexes

complex type	$M:O_2$	structure	metal ion[a]	example(s)[b]	ref
superoxo	1:1	4	Co(II)/Co(III)	$Co(ACACEN)(PYR)O_2$	139, 394, 399
				$Co(PPIXDME)(PYR)O_2$	403, 421
				$[Co(CN)_5O_2]^{3-}$	208, 209
				CoMb	396, 421, 449, 463, 464
			Fe(II)/Fe(III)	hemoglobin	26
				myoglobin	26
				$Fe(TPivPP)(N\text{-}MeIm)O_2$	177, 313
				Fe(octaaza[14]annulene)$(PYR)O_2$	136, 137
				Fe[pyrroheme *N*-[3-(1-imidazolyl)propyl]amide]	138
			Mn(II)/Mn(III)	Mn(X-SALDPTZ) (X = 5-NO_2, 5-H, 5-CH_2O, 3-NO_2, 3-OCH_3)	385
				$Mn(SALDAPE)O_2$	385
			Cr(II)/Cr(III)	$Cr(TPP)(PYR)O_2$	271
			Ru(II)/Ru(III)	$Ru(OEP)(CH_2CN)O_2$	272
			Ni(II)/Ni(III)	$Ni(DTAHD)O_2$	388
			Rh(II)/Rh(III)	$Rh(OEP)O_2$	273
			Rh(III)/Rh(III)	$[Rh(EN)_2(NO_2)(O_2)]^+$	274
	2:1	5	Co(II)/Co(III)	$[(Co(NH_3)_5)_2O_2]^{5+}$	187
				$[(Co(CN)_5)_2O_2]^{5-}$	210
				$[(Co(NH_3)_4)_2(O_2)(NH_2)]^{4+}$	112
				$[(Co(EN)_2)_2(O_2)(OH)]^{4+}$	195
			Cu(I)/Cu(II)	$Cu_2O_2(PYR)_X$[c]	275
			Rh(II)/Rh(III)	$[(Rh(L)_4Cl)_2O_2]^{3+}$ (L = PYR or PIC)	276, 277
peroxo	1:1	6	Ru(0)/Ru(II)	$Ru(PPh_3)_2(CO)_2O_2$	278
			Ru(I)/Ru(III)	$Ru(PPh_3)_2(NO)(Br)O_2$	279
			Os(0)/Os(II)	$Os(PPh_3)_2(CO)_2O_2$	278
			Co(I)/Co(III)	$[Co(Ph_2PCH{=}CHPPh_2)_2O_2]^+$	225
				$[Co(pyridylamine)_2O_2]^+$	280
				$[Co(FARS)O_2]^+$	281
			Rh(I)/Rh(III)	$[RhL_4O_2]^+$ (L = $PPh(CH_3)_2$ or $AsPh(CH_3)_2$	282, 283
			Ir(I)/Ir(III)	$Ir(PPh_3)_2(CO)Cl(O_2)$	174
				$Ir(PPh_2R)_3(CO)O_2$	284
			Ni(0)/Ni(II)	NiL_2O_2 (L = $CNC(CH_3)_3$, CNC_6H_{11})	285, 286
			Pd(0)/Pd(II)	$Pd(CNC(CH_3)_3)O_2$	285, 286
			Pt(0)/Pt(II)	$Pt(PPh_3)_2(O_2)$	285, 286
			Ti(0)/Ti(II)	$Ti(OEP)O_2$	287, 288
			Mo(0)/Mo(II)	$Mo(TPP)O_2$	289
			Co(II)/Co(IV)	$Co_2(CN)_4(PMe_2Ph)_5(O_2)$	150
			V	$[VO(O_2)_2(NH_3)]^+$	190-292
			Nb	$[Nb(O_2)_3(PHEN)]^-$	293-295
			Cr	$Cr(O)(O_2)_2L_3$ (L = NH_3, CN^-, PHEN)	296-298
			W	$[WO(O_2)_2(H_2O)_2O]$	299
			U	$[UO_2(O_2)_3]^{4-}$	300
			Mn(II)/Mn(IV)	$Mn(TPP)O_2$	301
	2:1	5	Co(II)/Co(III)	$[(Co(NH_3)_5)_2O_2]^{4+}$	186, 191, 192
				$[(Co(PYDIEN)_2O_2]^{4+}$	206, 207
				DL-$[(Co(EN)_2)_2O_2(NH_2)]^{3+}$	198
				$[(Co(EN)_2)_2O_2(OH)]^{3+}$	195-197
			Fe(II)/Fe(III)	hemerythrin	22
				$[Fe(tetrasulfophthalocyanine)]_2O_2$	303-305, 378, 379
			Cu(I)/Cu(II)	hemocyanin	31
				$[(Cu(BIMP))_2O_2]$	389
			Rh(II)/Rh(III)	$[Rh(OEP)]_2O_2$	273
				$[(Ru(EDTA))_2O_2]$	306
			Pd(I)/Pd(I)[d]	$[Pd(MeO\text{-}BHCP)(CH_3CN)]_2O_2$	317
			Pd(I)/Pd(I)[d]	$[Pd(RO\text{-}BHCP))_2O_2]$	317
			Rh	$\{RhClO_2[P(C_6H_5)]_2\}_2$	307
			Rh(I)/Rh(I)	$(RhL)_2O_2$ (L = COD, BHD)	308
			Mo	$[Mo_4O_{12}(O_2)_2]^{4-}$	309
				$[Mo_7O_{22}(O_2)_2]^{6-}$	310
			Cu	$Cu_4Cl_4L_3O_2$ (L = PYR, 4-PIC, 2,4-lutidine, BPY)	311

[a] Oxidation state prior to oxygenation reaction is given first, followed by the oxidation state subsequent to oxygenation reaction. [b] In view of the many compounds appearing in the literature, only selected examples are given. For more examples the references should be consulted. [c] Reaction is $4Cu(I) + O_2(PYR) \rightarrow 2Cu(II) + Cu_2O_2(PYR)_X$. [d] From reaction with KO_2.

stant solvents,[145,366-369] dilute solutions, or complexes in which steric hindrance prevents bridge formation.[370,372] There is good evidence for the formation of binuclear μ-superoxo or μ-peroxo complexes from the mononuclear superoxo precursors. Oxygenation of $Co(CN)_5^{3-}$ in DMF and of $Co(s\text{-}Me_2EN)_2Cl_2$ in EtOH

yield stable mononuclear complexes.[209,372b] However, in H_2O, a higher dielectric constant solvent, oxygenation results in the generation of μ-peroxo compounds,[211,323] Contrasting this behavior is the reaction between two $[Co(CN)_5O_2]^{3-}$ centers in H_2O giving the binuclear μ-superoxo adduct as studied by EPR.[372c] This is essentially a superoxide displacement reaction as indicated in eq 6. Resonance Raman studies of the oxygenation

$$2[Co(CN)_5O_2]^{3-} \rightarrow [Co_2(CN)_{10}(O_2)]^{5-} + O_2^{-}\cdot \quad (6)$$

of (3,10-diacetyl-2,11-dihydroxy-5,8-diaza-2,4,8,10-dodecatetraene)cobalt(II), Co(J-EN), in various organic solvents and under different pressures of dioxygen show reversible formation of 1:1 and 2:1 adducts.[368] In this particular system the 1:1 superoxo complex is favored in a polar aprotic solvent, CH_3CN (ϵ = 37.5 at 20 °C, μ = 3.37 D), at high dioxygen pressure and low temperature while the 2:1 peroxo complex dominates in a less polar aprotic solvent, CH_2Cl_2 (ϵ = 9.08 at 20 °C, μ = 1.54 D), at lower dioxygen pressure and higher temperature.[368] In Fe(II) complexes, μ-peroxo bridge formation is followed immediately by an irreversible reduction to form a μ-oxo-bridged complex.[373-376] Ochiai[377] has offered the following explanation for this behavior. Formation of μ-oxo-metal dimers may be represented by a series of equilibria as indicated in eq 7-10.[377] In comparison, although the reduction of

$$M^{n+}L + O_2 \rightleftharpoons M^{n+1}LO_2^{-} \quad (7)$$

$$M^{n+1}LO_2^{-} + M^{n+}L \rightleftharpoons M^{n+1}LO_2^{2-}M^{n+1}L \quad (8)$$

$$M^{n+1}LO_2^{2-}M^{n+1}L \rightleftharpoons 2M^{n+1}LO^{-}\cdot \quad (9)$$

$$M^{n+1}LO^{-}\cdot + M^{n+}L \rightleftharpoons M^{n+1}LO^{2-}M^{n+1}L \quad (10)$$

dioxygen to H_2O (eq 11) is thermodynamically more favorable than its partial reduction to H_2O_2 (eq 12),

$$^1/_2H^+ + {}^1/_4O_2 + e^- \rightarrow {}^1/_2H_2O$$

$$\Delta G^\circ{}_{25}{}^{pH7} = -74.7 \text{ kcal mol}^{-1} \quad (11)$$

$$H^+ + {}^1/_2O_2 + e^- \rightarrow {}^1/_2H_2O_2$$

$$\Delta G^\circ = -12.2 \text{ kcal mol}^{-1} \quad (12)$$

rupture of the O–O bond requires 51.1 kcal mol^{-1}. As illustrated in the potential energy vs. reaction coordinate diagram (Figure 6a) the formation of a μ-oxo–metal dimer would require lowering an intermediate potential barrier. Stabilization of the $M^{n+1}LO^{-}\cdot$ intermediate would allow for this. The simple molecular orbital diagram (Figure 6b) shows that the important interaction between the metal dπ orbital and the oxygen p orbital generates both a bonding (χ_1) and antibonding (χ_2) molecular orbital.[377] For metal ions with d^n configuration with $n < 5$ the $M^{n+1}LO^{-}\cdot$ is predicted to be stable. However, for $n > 5$ the additional electrons must populate antibonding (i.e., χ_2) orbitals and therefore would be predicted to be higher energy species. One additional condition must be met. There must be free $M^{n+1}L$ available to react with $M^{n+1}LO^{-}$. This situation will exist if the equilibrium constants for (7), (8), and (9) are small or if the rates of formation for eq 7-9 are much slower than for eq 10.

Because of the kinetic instability of the μ-peroxo

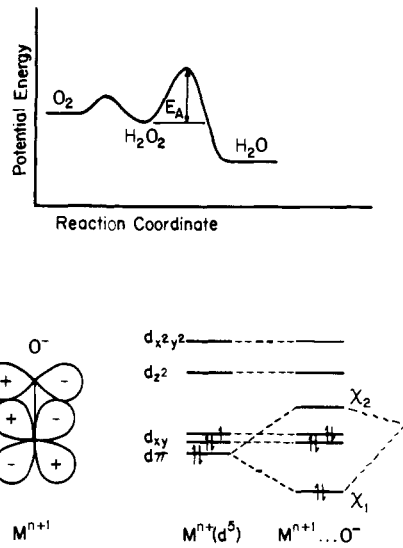
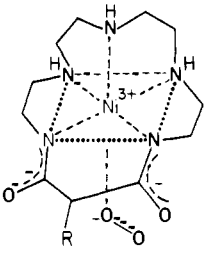


Figure 6. (Top) Potential energy plotted for the reduction of dioxygen to water with respect to reaction coordinate. (Bottom) Orbital overlap and qualitative molecular orbital diagram for $M^{n+1}O^{-}$.

binuclear complexes, Fe(II) dioxygen complexes have in general been limited to 1:1 $Fe^{III}O_2$(-I,0) complexes;[177-179] hemoglobin (HbO_2) and oxymyoglobin (MbO_2) are included in this class. The notable exceptions to this rule are hemerythrin (14) and the tetrasulfophthalocyanine iron(II) dioxygen adduct.[302,303,378,379]



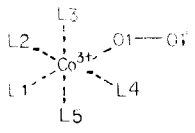
14

The latter compound is extremely susceptible to irreversible oxidation, normally being observed only as an intermediate in the oxidation of the iron(II) complex;[378] however, it has been isolated in the solid state where it is apparently stable.[370] It is probable that further oxidation is *sterically* prevented in the solid state. Very recent work has demonstrated that Fe(II) complexes with macrocyclic ligands can form stable dioxygen complexes in aqueous and nonaqueous solutions.[380-382] The most exciting of these new ligands is 3,6,10,13,19-pentaazabicyclo[13.3.1]-1(19),15,17-nonadecatriene. Both the Fe(II) and Co(II) chelates will reversibly bind dioxygen in aqueous solution to form μ-peroxo binuclear complexes. Although the Fe(II) analogue is stable enough for potentiometric determination of its oxygenation constant, there is a slow decomposition reaction which occurs, generating the more thermodynamically stable μ-oxo–Fe(III) dimer. Additional work on the formation of the violet intermediate dioxygen complex [λ_{max} 540 nm (ϵ 187)] from the oxygenation of the initial yellow Fe(II) chelate closely parallels that of oxyhemerythrin [λ_{max} 500 nm (ϵ 140)/$(Fe)_2O_2$]. Both of these absorption bands can be reasonably assigned to Fe(III) ← O_2^{2-} LMCT.

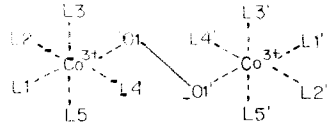
Both the μ-peroxo and the superoxo complexes dis-

TABLE VIII. Selected Bond Distances (Å), Bond Angles (deg), and Crystal Structure Data for Cobalt Dioxygen Complexes

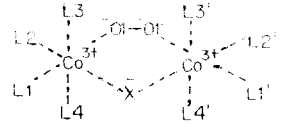
A. Amines and Cyanides



mononuclear



binuclear monobridged

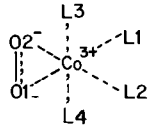


binuclear dibridged

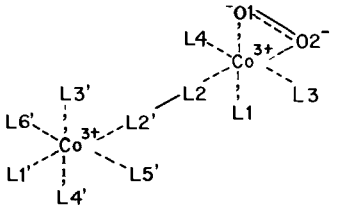
compound	Co-L1	Co-L2	Co-L3	Co-L4	Co-L5	Co-O1	O1-O1'	Co-Co'	Co-O1-O1'	
1. mononuclear, superoxo										
$[N(C_2H_5)_4]_3[Co(CN)_5O_2]\cdot 5H_2O$	1.903 (12)	1.888 (11)	1.887 (11)	1.909 (12)	1.957 (12)	1.904 (14)	1.240 (17)		153.4	
2. binuclear monobridged, superoxo										
$[(Co(NH_3)_5)_2O_2](NO_3)_5$	1.955 (2)	1.968 (2)	1.946 (2)	1.955 (2)	1.968 (2)	1.895 (2)	1.317 (2)	4.545 (3)	117.3 (20)	
$[(Co(NH_3)_5)_2O_2](SO_4)(HSO_4)$,	1.969 (30)	1.933 (30)	1.968 (30)	1.958 (30)	1.903 (30)	1.894 (30)	1.312 (30)	4.562 (20)	117.8 (20)	
	1.946 (30)	1.951 (30)	1.955 (30)	1.931 (30)	1.947 (30)	1.894 (30)			117.5 (20)	
$[(Co(NH_3)_5)_2O_2](HSO_4)(SO_4)_2\cdot 3H_2O$	1.937 (8)	1.946 (8)	1.953 (8)	1.926 (8)	1.983 (8)	1.904 (7)	1.272 (9)		116.7 (4)	
	1.959 (8)	1.937 (8)	1.959 (7)	1.954 (8)	1.971 (8)	1.890 (7)	1.270 (10)		117.5 (4)	
$K_5[(Co(CN)_5)_2O_2]\cdot H_2O$	1.826 (15)	1.899 (15)	1.864 (15)	1.881 (15)	1.868 (15)	1.919 (9)	1.289 (20)	4.634 (8)	120.7 (10)	
	1.851 (15)	1.886 (15)	1.891 (15)	1.862 (15)	1.900 (15)	1.954 (9)	1.243 (13)	4.637 (6)	120.6 (6)	
	1.850 (15)	1.889 (15)	1.880 (15)	1.872 (15)	1.864 (15)	1.934 (9)			121.8 (7)	
binuclear monobridged, peroxo										
$[(Co(NH_3)_5)_2O_2](SCN)_4$	1.971 (7)	1.947 (4)	1.947 (4)	1.963 (4)	1.963 (4)	1.879 (3)	1.469 (6)		110.8 (?)	
$[(Co(NH_3)_5)_2O_2](SO_4)_2\cdot 4H_2O$	1.985 (9)	1.961 (9)	1.964 (9)	1.951 (9)	1.947 (9)	1.876 (7)	1.473 (10)	4.427 (2)	113.2 (10)	
	1.981 (9)	1.952 (9)	1.966 (9)	1.960 (9)	1.953 (9)	1.889 (7)				
$[(Co(NH_3)_5)_2O_2](NO_3)_4\cdot 2H_2O$	2.000 (5)	1.981 (5)	1.969 (9)	1.959 (5)	1.991 (5)	1.886 (4)	1.472 (6)	4.512 (2)	110.9 (2)	
$[(Co(EN)_2(NO_2))_2O_2](NO_3)_2\cdot 4H_2O$	1.940 (8)	1.947 (8)	1.927 (7)	1.953 (7)	1.960 (7)	1.887 (6)	1.529 (9)		110.0 (6)	
$[(Co(EN)(DIEN))_2O_2](ClO_4)_4$	1.998 (4)	1.943 (4)	1.941 (4)	1.976 (4)	1.948 (4)	1.896 (4)	1.488 (6)		110.0 (3)	
$[(Co(PAPD))_2O_2](S_2O_6)(NO_3)_2\cdot 4H_2O$	1.988 (6)	1.971 (6)	1.979 (7)	1.997 (6)	1.976 (8)	1.924 (5)	1.486 (7)	4.612	111.9 (4)	
$[(Co(PYDPT))_2O_2]I_4\cdot 3H_2O$	2.006 (8)	1.964 (8)	1.945 (8)	1.948 (9)	2.002 (7)	1.888 (6)	1.456 (9)		115.40 (46)	
	2.009 (8)	1.986 (8)	1.928 (7)	1.982 (9)	1.958 (7)	1.894 (6)			114.34 (45)	
$[(Co(PYDIEN))_2O_2]I_4$	2.001 (6)	1.986 (8)	1.910 (7)	1.902 (8)	1.954 (7)	1.876 (4)	1.489 (8)		112.5 (4)	
$K_8[(Co(CN)_5)_2O_2](NO_3)_2\cdot 4H_2O$	1.875 (4)	1.890 (4)	1.900 (3)	1.895 (4)	1.913 (3)	1.985 (3)	1.447 (4)		118.8 (3)	
3. binuclear dibridged, superoxo					Co-X					Co-L-Co'
$[(Co(NH_3)_4)_2(NH_2)(O_2)](NO_3)_4$	1.973 (5)	1.971 (5)	1.954 (5)	1.957 (5)	1.928 (4)	1.865 (4)	1.320 (5)	3.242 (1)	120.4 (3)	114.9 (2)
	1.952 (5)	1.989 (5)	1.952 (5)	1.944 (5)	1.916 (4)	1.869 (4)			121.3 (3)	
$[(Co(EN)_2)_2(NH_2)(O_2)](NO_3)_4\cdot H_2O$	1.963 (8)	1.984 (12)	1.952 (11)	1.946 (9)	1.908 (9)	1.885 (8)	1.353 (11)	3.276 (3)	118.9 (7)	115.5 (6)
	1.947 (11)	1.967 (9)	1.979 (11)	1.928 (9)	1.940 (8)	1.870 (9)			119.5 (6)	
$[(Co(EN)_2)_2(OH)(O_2)](NO_3)_4\cdot H_2O$	1.971 (10)	1.971 (10)	1.959 (10)	1.946 (10)	1.901 (10)	1.872 (10)	1.339 (10)	3.261 (10)	119.7 (?)	117.4 (?)
	1.959 (10)	1.955 (10)	1.968 (10)	1.936 (10)	1.917 (10)	1.875 (10)			120.0 (?)	
binuclear dibridged, peroxo										
$[(Co(EN)_2)_2(NH_2)(O_2H)](NO_3)_4\cdot 2H_2O$					1.94 (?)	1.92 (?)	1.42		119 (?)	100 (?)
					1.95 (?)	1.92 (?)			111 (?)	
$[(Co(EN)_2)_2(NH_2)(O_2)](SCN)_3\cdot H_2O$	1.977 (12)	1.997 (12)	1.964 (12)	1.932 (12)	1.928 (12)	1.873 (12)	1.458 (21)	3.276 (12)	110 (?)	114.8 (?)
	1.983 (12)	1.989 (12)	1.980 (12)	1.937 (12)	1.961 (12)	1.870 (12)			109 (?)	
$[(Co(EN)_2)_2(NH_2)(O_2)](NO_3)_3\cdot {}^{15}/_{8}AgNO_3\cdot H_2O$	1.99 (1)	1.99 (1)	1.97 (1)	1.98 (1)	1.95 (1)	1.88 (1)	1.43 (3)		110.9 (4)	114.6 (7)
$[(Co(EN)_2)_2(OH)(O_2)](S_2O_6)(NO_3)\cdot 2H_2O$	2.020 (20)	1.985 (20)	1.977 (20)	1.965 (20)	1.955 (20)	1.860 (20)	1.465 (20)	3.272 (20)	110.0 (?)	114.4 (?)
	2.018 (20)	1.987 (20)	1.959 (20)	1.978 (20)	1.943 (20)	1.865 (20)			110.6 ( )	
$[(Co(EN)_2)_2(OH)(O_2)](ClO_4)_3\cdot H_2O$	2.005 (11)	1.947 (13)	1.920 (12)	1.979 (12)	1.934 (10)	1.880 (8)	1.460 (13)	3.289 (?)	108.3 (6)	117.2 (4)
	1.999 (13)	1.974 (10)	1.946 (13)	1.930 (13)	1.919 (8)	1.866 (10)			110.2 (6)	
$[(Co(EN)_2)_2(OH)(O_2)]I_3\cdot 4.5H_2O$	2.00 (4)	1.90 (4)	1.95 (4)	1.91 (4)	1.87 (3)	1.84 (4)	1.45 (6)		110 (3)	119 (2)
	1.93 (5)	1.97 (4)	1.89 (5)	1.80 (5)	1.89 (3)	1.74 (4)			116 (3)	
$[(Co(TREN))_2(OH)(O_2)](ClO_4)_3\cdot H_2O$	1.915 (26)	1.995 (25)	1.967 (26)	2.016 (26)	1.970 (23)	1.857 (18)	1.462 (26)	3.292 (?)	112.1 (12)	117.9 (12)

	1.948 (29)	2.014 (27)	1.967 (21)	2.004 (34)	1.872 (23)	1.869 (20)			109.4 (14)	
$[(Co(TREN))_2(TREN)(O_2)](ClO_4)_4 \cdot 2H_2O$	2.023 (19)	1.956 (16)	1.995 (23)	1.965 (22)	2.016 (15)	1.877 (16)	1.485 (25)	4.574 (12)	116.5 (12)	
	1.958 (23)	1.936 (23)	1.979 (36)	1.935 (26)	2.143 (28)	1.914 (17)			115.1 (13)	
$[(Co(DMTAD))_2(OH)(O_2)](ClO_4)_3 \cdot 2H_2O$	2.043 (17)	1.841 (22)	2.066 (18)	1.923 (18)	1.934 (19)	1.946 (14)	1.429 (20)	3.321	109.9 (10)	115.8 (5)
	2.035 (19)	2.072 (13)	2.068 (18)	1.866 (19)	1.987 (19)	1.843 (15)			107.3 (10)	

B. Arsines and Phosphines



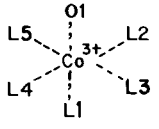
mononuclear peroxo (type 1)



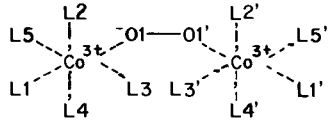
mononuclear peroxo (type 2)

compound	Co-L1	Co-L2	Co-L3	Co-L4	Co-L5	Co-L6	Co-O1	Co-O2	O1-O2	O1-Co-O2
1. mononuclear, peroxo (type 1)										
$[Co(As_4C_{24}H_{38})(O_2)]ClO_4$	2.292 (2)	2.314 (2)	2.299 (2)	2.320 (2)			1.862 (6)	1.867 (7)	1.424 (11)	44.9 (3)
$[Co(2\text{-}PHOS)_2(O_2)]BF_4$	2.246 (3)	2.238 (3)	2.232 (3)	2.251 (3)			1.902 (7)	1.871 (7)	1.420 (10)	
2. mononuclear, peroxo (type 2)										
$[(Co(CN)_2(PMe_2Ph)_3(CN)Co(PMe_2Ph)_2\text{-}$	1.913 (15)	1.851 (12)	2.244 (4)	2.208 (4)			1.910 (9)	1.888 (9)	1.441 (11)	44.6 (3)
$(CN)(O_2)] \cdot {}^1/_2C_6H_6$	2.226 (4)	1.916 (10)	2.285 (4)	2.309 (4)	1.880 (13)	1.881 (11)				

C. Schiff Bases



mononuclear



binuclear monobridged

compound	Co-L1	Co-L2	Co-L3	Co-L4	Co-L5	Co-O1	O1-O1'	Co-Co'	Co-O1-O1'
1. mononuclear									
$[Co(BENACEN)(PYR)(O_2)$	2.02 (?)					1.86 (?)	1.26 (4)		126 (2)
$[Co(ACACEN)(O_2)]PYR$						1.95 (5)			
$[Co(SALTMEN)(BzIm)(O_2)] \cdot THF$	2.011 (2)	1.889 (2)	1.896 (2)	1.894 (2)	1.899 (2)	1.889 (2)	1.277 (3)		120.0 (2)
$[Co(3\text{-}t\text{-}BuSALTMEN)(BzIm)(O_2)] \cdot 1.5ACE$	1.966 (7)	1.879 (6)	1.882 (8)	1.909 (8)	1.911 (6)	1.882 (6)	1.273 (10)		117.5 (6)
						1.974 (8)	1.257 (10)		118.5 (6)
$[Co(3\text{-}F\text{-}SALTMEN)(N\text{-}MeIm)(O_2)] \cdot 2ACE$	2.004 (2)	1.907 (2)	1.896 (2)	1.890 (2)	1.895 (2)	1.881 (2)	1.302 (3)		117.4 (?)
$[Co(SALTMEN)(O_2)] \cdot MeCN$	2.029 (22)	1.882 (16)	1.889 (22)	1.868 (21)	1.898 (16)	1.90 (3)	1.06 (3)		
$[Co(3\text{-}MeO\text{-}SALTMEN)(H_2O)(O_2)] \cdot DME$	2.048 (5)	1.909 (3)	1.896 (4)	1.898 (4)	1.901 (3)	1.88 (1)	1.25 (2)		117 (1)
$[Co(3\text{-}t\text{-}BuSALEN)(PYR)(O_2)]$	2.018 (6)	1.900 (6)	1.890 (6)	1.883 (6)	1.897 (5)	1.870 (6)	1.350 (11)		116.4 (5)
$[Co(SALMDPT)(O_2)][Co(SALMDPT)] \cdot 2Bz$	2.09 (3)	1.91 (2)	1.90 (2)	1.93 (2)	2.00 (2)	1.88 (2)	1.06 (5)		135 (4)
2. binuclear monobridged									
$[Co(H_2O)(3\text{-}FSALEN)(O_2)(Co(3\text{-}FSALEN))]_2 \cdot$	2.193 (?)	1.990 (?)	1.901 (?)	1.922 (?)	1.903 (?)	1.931 (30)	1.308 (28)		117 (?)
$(CHCl_3)_2 \cdot PIP$	2.196 (?)	1.904 (?)	1.866 (?)	1.899 (?)	1.884 (?)	2.000 (30)			119 (?)
$[(Co(SALDPT))_2(O_2)] \cdot C_6H_5CH_3$	1.91 (1)	1.89 (1)	1.96 (1)	1.99 (1)	1.92 (1)	1.93 (1)	1.45 (1)	4.65 (5)	118.5 (?)
$[(Co(SALEN)(DMF))_2(O_2)]$	2.150 (7)	1.900 (5)	1.894 (7)	1.872 (6)	1.903 (6)	1.910 (6)	1.339 (6)		120.3 (2)
$[(Co(SALEN)(PIP))_2(O_2)] \cdot {}^1/_3PIP \cdot {}^2/_3ACE$	2.101 (5)	1.917 (5)	1.850 (5)	1.888 (5)	1.901 (5)	1.909 (5)	1.383 (7)		120.5 (4)
	2.131 (5)	1.909 (5)	1.854 (5)	1.909 (5)	1.887 (5)	1.914 (5)			119.6 (4)

TABLE VIII (*Continued*)

D. Crystal Structure Data

compound	crystal systems and unit cell parameters[a]		temp	ref
$[(NH_3)_5CoO_2Co(NH_3)_5](NO_3)_5$	tetragonal	$a = 11.961$ (4), $c = 8.078$ (1) Å	NG (RT)	187
$[(NH_3)_5CoO_2Co(NH_3)_5](SO_4)(HSO_4)_3$	orthorhombic	$a = 16.360$ (1), $b = 13.946$ (3), $c = 9.978$ (1) Å	NG (RT)	188, 189
$[(NH_3)_5CoO_2Co(NH_3)_5](SCN)_4$	orthorhombic	$a = 13.266$ (2), $b = 10.574$ (2), $c = 7.940$ (2) Å	NG (RT)	186, 191
$[(NH_3)_5CoO_2Co(NH_3)_5](HSO_4)(SO_4)_2 \cdot 3H_2O$	monoclinic	$a = 13.392$ (3), $b = 9.742$ (3), $c = 17.709$ (7) Å, $\beta = 100.98$ (2)°	NG (RT)	190
$[(NH_3)_5CoO_2Co(NH_3)_5](SO_4)_2 \cdot 4H_2O$	monoclinic	$a = 7.614$ (2), $b = 29.672$ (5), $c = 9.595$ (1) Å, $\beta = 96.97$ (1)°	22 °C	192
$[(NH_3)_5CoO_2Co(NH_3)_5](NO_3)_4 \cdot 2H_2O$	monoclinic	$a = 11.657$ (5), $b = 11.977$ (6), $c = 8.082$ (4) Å, $\beta = 91.58$ (4)°	NG (RT)	193
$[(NH_2)_4Co(NH_2)(O_2)Co(NH_3)_4](NO_3)_4$	monoclinic	$a = 8.451$ (3), $b = 13.196$ (6), $c = 17.304$ (3) Å, $\beta = 103.90$ (3)°	26 °C	12
$[(EN)_2Co(OH)(O_2)Co(EN)_2](NO_3)_4 \cdot H_2O$	monoclinic	$a = 8.818$ (2), $b = 23.591$ (4), $c = 12.489$ (3) Å, $\beta = 96.08$ (5)°	NG (RT)	195
$[(EN)_2Co(NH_2)(O_2)Co(EN)_2](NO_3)_4 \cdot H_2O$	monoclinic	$a = 8.781$ (1), $b = 23.968$ (2), $c = 12.498$ (2) Å, $\beta = 95.80$ (1)°	NG (RT)	113, 194
$[(EN)_2Co(NH_2)(HO_2)Co(EN)_2](NO_3)_4 \cdot 2H_2O$	monoclinic	$a = 8.23$, $b = 15.41$, $c = 20.48$ Å, $\beta = 98.9$°	NG (RT)	113
$[(EN)_2Co(OH)(O_2)Co(EN)_2](S_2O_6)(NO_3) \cdot 2H_2O$	monoclinic	$a = 10.480$ (3), $b = 24.371$ (4), $c = 9.901$ (3) Å, $\beta = 94.37$ (4)°	NG (RT)	195
$[(EN)_2Co(OH)(O_2)Co(EN)_2](ClO_4)_3 \cdot H_2O$	monoclinic	$a = 19.280$ (5), $b = 11.984$ (3), $c = 11.654$ (3) Å, $\beta = 99.190$ (4)°	NG (RT)	196
$[(EN)_2Co(OH)(O_2)Co(EN)_2](I)_3 \cdot 4.5H_2O$	monoclinic	$a = 16.086$ (7), $b = 8.664$ (5), $c = 20.248$ (9) Å, $\beta = 97.74$ (3)°	NG (RT)	197
$[(EN)_2Co(NH_2)(O_2)Co(EN)_2](SCN)_3 \cdot H_2O$	orthorhombic	$a = 26.766$ (2), $b = 12.727$ (1), $c = 14.461$ (1) Å	24 (2) °C	198
$[NO_2(EN)_2CoO_2Co(EN)_2NO_2](NO_3)_2 \cdot 4H_2O$	monoclinic	$a = 10.755$ (11), $b = 12.941$ (8), $c = 9.709$ (6) Å, $\beta = 100.4$ (1)°	NG (RT)	200
$[(EN_2)Co(NH_2)(O_2)Co(EN)_2](NO_3)_3 \cdot {}^{15}/_{8}AgNO_3 \cdot H_2O$	monoclinic	$a = 8.710$ (3), $b = 16.413$ (5), $c = 20.024$ (8) Å, $\beta = 90.30$ (4)°	NG (RT)	199
$[(EN)(DIEN)CoO_2Co(EN)(DIEN)](ClO_4)_4$	monoclinic	$a = 9.062$ (2), $b = 15.981$ (8), $c = 11.153$ (4) Å, $\beta = 92.53$ (3)°	NG (RT)	201
$[(TREN)Co(OH)(O_2)Co(TREN)](ClO_4)_3 \cdot 3H_2O$	orthorhombic	$a = 14.697$ (6), $b = 16.530$ (8), $c = 12.461$ (4) Å, (only 1 H_2O reported)	NG (RT)	202
$[(TREN)Co(TREN)(O_2)Co(TREN)](ClO_4)_4 \cdot 2H_2O$	monoclinic	$a = 9.798$ (4), $b = 26.385$ (12), $c = 16.385$ (7) Å, $\beta = 110.10$ (5)°	NG (RT)	203
$[(DMTAD)Co(OH(O_2)Co(DMTAD)](ClO_4)_3 \cdot 2H_2O$	orthorhombic	$a = 14.632$ (4), $b = 17.525$ (5), $c = 12.888$ (5) Å, (DMTAD ≡ DMTRIEN)	NG (RT)	204
$[(PAPD)CoO_2Co(PAPD)](S_2O_6)(NO_3)_2 \cdot 4H_2O$	triclinic	$a = 9.405$ (4), $b = 9.270$ (4), $c = 12.218$ (6) Å, $\alpha = 89.58$ (5), $\beta = 99.08$ (6)°, $\gamma = 114.79$ (5)°	NG (RT)	205
$[(PYDPT)CoO_2Co(PYDPT)]I_4 \cdot 3H_2O$	monoclinic	$a = 20.104$ (9), $b = 11.896$ (5), $c = 21.899$ (5) Å, $\beta = 116.33$ (10)°	NG (RT)	206
$[(PYDIEN)CoO_2Co(PYDIEN)]I_4$	orthorhombic	$a = 26.73$ (2), $b = 32.19$ (1), $c = 10.049$ (6) Å	NG (RT)	207
$[(C_2H_5)_4]_3[Co(CN)_5O_2] \cdot 5H_2O$	monoclinic	$a = 10.444$ (4), $b = 14.105$ (8), $c = 14.392$ (6) Å, $\beta = 108.63$ (2)°	23 °C	208, 209
$K_8[(CN)_5CoO_2Co(CN)_5](NO_3)_2 \cdot 4H_2O$	monoclinic	$a = 11.605$ (4), $b = 8.383$ (3), $c = 16.639$ (4) Å, $\beta = 109.43$ (2)°	NG (RT)	211
$K_5[(CN)_5CoO_2Co(CN)_5] \cdot H_2O$	triclinic	$a = 11.707$ (9), $b = 19.423$ (15), $c = 7.664$ (7) Å, $\alpha = 93.92$ (7), $\beta = 110.36$ (8)°, $\gamma = 94.71$ (8)°	NG (RT)	210
$[Co(O_2)As_4C_{24}H_{38}]ClO_4$	orthorhombic	$a = 12.595$ (7), $b = 20.937$ (10), $c = 11.509$ (6) Å	20 °C	226
$[(CH)_2(PMe_2Ph)_3CoCNCo(PMe_2Ph)_2(CN)(O_2)] \cdot {}^{1}/_{2}C_6H_6$	orthorhombic	$a = 33.583$ (4), $b = 30.471$ (4), $c = 19.449$ (2) Å	NG (RT)	156
$[Co(O_2)(2\text{-}PHOS)_2]BF_4$	monoclinic	$a = 16.034$ (6), $b = 18.186$ (9), $c = 19.721$ (8) Å, $\beta = 101.20$ (1)°	NG (RT)	225
$[(H_2O)(3\text{-}F\text{-}SALEN)CoO_2Co(3\text{-}F\text{-}SALEN)]_2(CHCl_3)_2 \cdot (C_5NH_{11})$	triclinic	$a = 12.937$ (4), $b = 14.806$ (3), $c = 14.866$ (9) Å, $\alpha = 118.42$ (9), $\beta = 112.28$ (15)°, $\gamma = 107.89$ (4)°	NG (RT)	220
$[(DMF)(SALEN)CoO_2Co(SALEN)(DMF)]$	monoclinic	$a = 28.85$ (4), $b = 12.94$ (2), $c = 11.32$ (2) Å, $\beta = 118.7$ (3)°	NG (RT)	222, 223
$[(SALDPT)CoO_2Co(SALDPT)] \cdot C_6H_5CH_3$	monoclinic	$a = 10.236$ (7), $b = 24.21$ (2), $c = 18.02$ (1) Å, $\beta = 104.06$ (6)°	NG (RT)	221
$[Co(BENACEN)(PYR)O_2]$	orthorhombic	$a = 13.69$ (7), $b = 8.215$ (9), $c = 21.88$ (6) Å	NG (RT)	214a
$[Co(ACACEN)(O_2)]PYR$	monoclinic	$a = 8.87$ (2), $b = 16.73$ (3), $c = 13.82$ (3) Å, $\beta = 115.1$ (3)°	−40 °C	214b
$[(PIP)(SALEN)CoO_2Co(SALEN)(PIP)] \cdot 0.67ACE \cdot 0.33PIP$	orthorhombic	$a = 17.262$ (1), $b = 19.201$ (1), $c = 26.630$ (2) Å	NG (RT)	224
$[Co(3\text{-}F\text{-}SALEN)(N\text{-}MeIm)O_2] \cdot 2ACE$	monoclinic	$a = 11.934$ (6), $b = 13.864$ (5), $c = 18.018$ (8) Å, $\beta = 92.35$ (2)°	−171 °C	215
$[Co(SALTMEN)(BzIm)(O_2)] \cdot THF$	monoclinic	$a = 11.485$ (1), $b = 14.566$ (1), $c = 19.102$ Å, $\beta = 93.60$°	NG (RT)	212
$[(3\text{-}t\text{-}BuSALTEN)(BzIm)(O_2)] \cdot {}^{1}/_{5}ACE$	monoclinic	$a = 11.918$ (1), $b = 21.331$ (5), $c = 17.267$ (2) Å, $\beta = 108.89$ (1)°	RT	213
	monoclinic	$a = 11.933$ (4), $b = 21.238$ (11), $c = 17.004$ (2) Å, $\beta = 109.86$ (3)°	−152 °C	213
$[Co(SALPEEN)(O_2)] \cdot MeCN$	monoclinic	$a = 9.563$ (2), $b = 19.490$ (4), $c = 12.770$ (3) Å, $\beta = 106.04$ (2)°	NG (RT)	216
$[Co(3\text{-}OMe\text{-}SALTMEN)(H_2O)(O_2)] \cdot DME$	monoclinic	$a = 10.918$ (1), $b = 20.035$ (1), $c = 13.442$ (1) Å, $\beta = 110.21$ (1)°	NG (RT)	217
$[Co(3\text{-}t\text{-}BuSALEN)(PYR)(O_2)]$	monoclinic	$a = 23.201$ (7), $b = 13.880$ (2), $c = 7.017$ (1) Å, $\beta = 98.10$ (2)°	NG (RT)	218
$[Co(SALMDPT)(O_2)][Co(SALMDPT)] \cdot 12Bz$	triclinic	$a = 17.045$ (4), $b = 12.697$ (3), $c = 11.668$ (3) Å, $\alpha = 94.23$ (3), $\beta = 90.06$ (3)°, $\gamma = 100.43$ (3)°	NG (RT)	219

[a] Cell parameters are temperature dependent; therefore data collection temperature is given. For those not given (NG), room temperature (23 ± 5 °C) is assumed.

cussed above have a bent M–O–O linkage (structures 4 and 5, respectively). The peroxo complexes formed when the d^8 metals (Pt(0), Pd(0), Ni(0), Ir(I), Rh(I), and Co(I)) react with dioxygen are bound symmetrically in the Griffith mode, 6, as are the $Mn(TPP)O_2$ adducts.[383-387] There is no evidence for any intermediate in the formation of these complexes.[384] The most recent review of the chemistry of these complexes is the excellent paper by Vaska.[97]

A novel dioxopentaamine macrocyclic ligand complex of nickel(II) has recently been reported to bind dioxygen end-on as a 1:1 (metal:dioxygen) complex.[388] Reversible oxygenation is facilitated in 14 by the presence of two basal imide anions and an axial nitrogen donor. These donor groups serve to stabilize the generated Ni(III) cation and provide sufficient metal electron density to coordinate dioxygen, giving the $Ni^{III}O_2^-(-I,0)$ formalism. In addition, this complex activates dioxygen sufficiently to convert toluene to o- and p-cresol.[388]

Of the remaining complexes, only the 2:1 (metal:dioxygen) complexes formed by reaction of Cu(I) and dioxygen require mention at this point. These complexes are presumably related to hemocyanin[31] in structure and properties. One of the complexes contains two imidazolyl donors, two aliphatic imino donors, and one pyridyl donor per copper(I) ion. It loses 20% of its oxygen carrying capacity on each oxygenation/deoxygenation cycle. The other complex is a binuclear complex[389] and an "ear muff" or "wishbone"[357-360] type ligand containing both nitrogen and sulfur donors. Complete reversibility is claimed for this complex in the solid state.[389] Unfortunately, neither complex has been structurally characterized.

For a more thorough discussion of bonding modes, the extent of electron transfer from the metal ion to dioxygen and similar topics, the reader is referred to the more general reviews of dioxygen complex chemistry.[92-102] Precise structural parameters for those cobalt complexes for which X-ray crystal structures are available may be found in Table VIII of this review.

2. Reversibility and Stability of Dioxygen Complexes

Both reversible and irreversible dioxygen uptake are known. Reversible dioxygen complexes, or oxygen carriers, are those in which bound dioxygen can be removed by a change in temperature, partial pressure of oxygen gas, pH, or other conditions. Formation of the dioxygen complex may be considered to be reversible only if the original metal complex (the "oxygen carrier") is formed when dioxygen is removed. Reversible oxygen uptake has been observed from complexes in both the solid state[57,116,390] and in solution.[391-407]

Completely reversible oxygenation requires that a compound be able to undergo repeated oxygenation/deoxygenation cycles without appreciable loss of activity. Although a few completely reversible systems have been studied[57,116,390,393] most oxygen carriers gradually lose activity over several oxygenation/deoxygenation cycles, or when stored in the oxygenated form.[389,391,392,408] In general, this loss of activity is due to irreversible oxidation of the original metal complex to an inactive complex in which the metal is in a higher oxidation state.[409-414] This reaction occurs with loss of the dioxygen ligand, either as peroxide[415,416] or as oxygenation products[32-35,92,93] or oxidation products in which the oxygen is reduced to water and the chelating ligand is oxidized.[417] Resistance toward this type of irreversible oxidation is often referred to in the literature as "stability". It is important to distinguish between resistance to irreversible oxidation and thermodynamic stability. In this paper "stability" will refer to the thermodynamic stability of the dioxygen complex which is a measure of the difference in free energies of the precursor complex and dioxygen relative to the dioxygen complex.

Stability may be expressed in terms of a stability constant, which is simply the equilibrium constant for the reaction between a metal complex and dioxygen (eq 13 or 14). The stability constant may be expressed in

$$ML_n + O_2 \overset{K_{O_2}}{\rightleftharpoons} ML_nO_2 \quad (13)$$

$$2ML_n + O_2 \overset{K_{O_2}}{\rightleftharpoons} (ML_n)_2O_2 \quad (14)$$

terms of dioxygen concentration or partial pressure of oxygen gas, as shown in eq 15 and 16. When exactly

$$K_{O_2} = \frac{[ML_nO_2]}{[ML_n][O_2]} \text{ or } K_{O_2} = \frac{[ML_nO_2]}{[ML_n]P_{O_2}} \quad (15)$$

$$K_{O_2} = \frac{[(ML_n)_2O_2]}{[ML_n]^2[O_2]} \text{or } K_{O_2} = \frac{[(ML_n)_2O_2]}{[ML_n]^2P_{O_2}} \quad (16)$$

half of the metal complex ML_n is oxygenated $[ML_n]_{1/2} = {}^1/_2[ML_n]_0$ and $[ML_nO_2]_{1/2} = {}^1/_2[ML_n]_0$ (eq 15) or $[ML_n]_{1/2} = {}^1/_2[ML_n]_0$ and $[(ML_n)_2O_2]_{1/2} = {}^1/_4[ML_n]_0$, the expressions for K_{O_2} reduce to eq 17 and 18, where $[ML_n]_0$ is the initial concentration of metal complex.

$$K_{O_2} = (P_{1/2})^{-1} \quad \text{for mononuclear complexes} \quad (17)$$

$$K_{O_2} = (P_{1/2}[ML_n]_0)^{-1} \quad \text{for binuclear complexes} \quad (18)$$

When stability constants are expressed as the dioxygen pressure at half-oxygenation ($P_{1/2}$), the stability constant increases as the $P_{1/2}$ decreases. In other words, the more stable the oxygen complex the lower is the dioxygen concentration required for its formation.

Table IX gives an indication of the range of stabilities exhibited by various types of dioxygen complexes. It is a truly remarkable range, covering nearly 12 orders of magnitude. One of the complexes shown ($Co(TPivPP)(Me_2Im)^{2+}$) is less than half saturated under a full atmosphere of pure dioxygen gas. Another complex $Co(TETREN)^{2+}$ will bind dioxygen in a solution containing only nanogram quantities of dioxygen. With such a wide variety of oxygen carrier stabilities, it should be possible to design one with the appropriate stability for any given application. Since many factors such as pH, solvent, metal ion, and coordinated ligands influence dioxygen complex formation equilibria, consideration of the oxygenation constant alone is insufficient to predict its behavior in solution.

Most of the equilibrium constants reported for Co(II) systems are expressed in terms of species concentration. For meaningful comparisons with other data, especially those for biomolecules, all constants have been reported in Table IX as constants of the form $K_{O_2} = (P_{1/2})^{-1}$. This is preferable to reporting $P_{1/2}$ directly, since $(P_{1/2})^{-1}$ varies directly rather than inversely with the dioxygen

TABLE IX. Comparison of Stabilities of Various Types of Dioxygen Complexes

oxygen-free complex	dioxygen complex	$P_{1/2}^{-1}$, atm^{-1}	conditions[a]	ref
human hemoglobin A, Hb	HbO_2 (FeO_2)	4.0×10^2	25 °C, pH 7.4 (TRIS buffer)	434, 437, 438
human hemoglobin A, Hb	HbO_2 (FeO_2)	5.0×10^1	25 °C, pH 7.4 (TRIS buffer), 0.002 M 2,3-DPG	434, 437
human hemoglobin A, Hb	HbO_2 (FeO_2)	1.5×10^1	25 °C, pH 7.4 (TRIS buffer), 0.002 M IHP	438
hemerythrin, Hry	$HryO_2$ (FeO_2Fe)	2.6×10^2	20 °C, pH 6.25 (unbuffered)	458
hemocyanin, Hcy	$HcyO_2$ (CuO_2Cu)	1.3×10^2	20 °C, pH 6.5	459
leghemoglobin, Lgb	$LgbO_2$	1.7×10^4	25 °C, pH 6.5 0.1 M phosphate	460
$FeTPivPP(Me_2Im)^{2+}$, MLL'	$MLL'O_2$	2.0×10^1	25 °C, toluene	425
$FeTPivPP(1\text{-}MeIm)^{2+}$, MLL'	$MLL'O_2$	2.5×10^3	20 °C, solid	313
$CoTPivPP(Me_2Im)^{2+}$, MLL'	$MLL'O_2$	8.4×10^{-1}	25 °C, toluene	425
Co(SALEN), ML	MLO_2	2.3	20 °C, Me_2SO	395
Co(ACACEN)Py, MLL'	$MLL'O_2$	4.0×10^2	−31 °C, toluene	399
$Co(3\text{-}F\text{-}SALEN)^{2+}$, ML	$(ML)_2O_2$	$\sim 3.8 \times 10^2$	25 °C, solid	116
$Co(TETREN)^{2+}$, ML	$(ML)_2O_2$	9.1×10^9	25 °C, $\mu = 0.10$	334, 581, 582
$Co(TREN)^{2+}$, ML	$(ML)_2O_2OH$	3.4×10^5	25 °C, $\mu = 0.10$, pH 7.0	362
$Co(TERPY)(BPY)^{2+}$, MLL'	$(MLL')_2O_2$	18	25 °C, $\mu = 0.10$	148, 581
$Co_2(BISTREN)OH^{3+}$, M_2LOH	$(M_2L)O_2(OH)$	3.5×10^{-2}	25 °C, $\mu = 0.10$, pH 7.0	359
$Mn(Me_2PPh)Br_2$, MLX_2	MLX_2O_2	$\sim 2.5 \times 10^2$	25 °C, solid[c]	57
$Mn(Bu_3P)(NCS)_2$, MLX_2	MLX_2O_2	~6.3	25 °C, solid[c]	57

[a] The abbreviations employed here and elsewhere are explained in the glossary. [b] Where solvent is not specified, the data were obtained in aqueous solution. [c] 25 °C is assumed. The temperature was not given in the reference cited.

affinity. Conversion of data to this form requires certain assumptions that may introduce slight approximations into the oxygenation constants. These are, however, small compared to the differences in the oxygenation constants which are under consideration. Although the examples given below apply to Co(II) monobridged and dibridged dioxygen complexes, equations for other systems may be derived in an analogous manner.

The major assumptions are that Henry's law[418] is valid for dioxygen in aqueous solutions at the ionic strengths normally employed and that for binuclear complex formation from mononuclear precursors, the concentration of the unoxygenated complex at $P_{1/2}$ is 1×10^{-3} M. Molarity and molality are assumed equivalent, introducing only a small error for aqueous solutions. The solubility of dioxygen in water at 25 °C under 1 atm of pressure is taken to 1.35×10^{-3} M.[419]

For the formation of a dibridged dioxygen complex (eq 19) the equilibrium constant is given by eq 20. The

$$2ML + O_2 \overset{K_{O_2}}{\rightleftharpoons} M_2L_2O_2(OH) + H^+ \quad (19)$$

$$K_{O_2} = \frac{[M_2L_2O_2(OH)][H^+]}{[ML]^2[O_2]} \quad (20)$$

equations for simple monobridged complexes were previously given (eq 14 and 16). At $P_{1/2}$, $[ML_n]_{1/2} = 1/2[ML_n]_0$ and $[(ML_n)_2O_2(OH)]_{1/2} = 1/4[ML_n]_0$ or $[(ML_n)_2O_2]_{1/2} = 1/4[ML_n]_0$. Thus at half-oxygenation, $P_{1/2}$ is given by eq 21 or 22, respectively. K_h is the Henry's law constant, which at 25 °C and 0.10 M ionic strength is numercially equal to 7.41×10^2 atm L mol^{-1}.

$$P_{1/2} = \frac{K_h[H^+]}{K_{O_2}[ML_n]_0} \quad (21)$$

$$P_{1/2} = \frac{K_h}{K_{O_2}[ML_n]_0} \quad (22)$$

For dibridged complexes, the $P_{1/2}$ value is pH dependent because of the hydrogen ion dependence of μ-hydroxo bridge formation. For this reason, the pH at which $P_{1/2}$ is calculated must be specified. A pH of 10.0 was selected as the standard for the dibridged dioxygen complexes discussed. Most of the equilibrium constants which have been reported for biomolecules are expressed as $P_{1/2}$. In these cases, only inversion of the constant was required.

The reaction of a complex with dioxygen generally involves a large negative entropy change which must be offset by a very favorable enthalpy if the free energy is to be negative. The large negative entropy results primarily from loss of rotational, vibrational, and translational freedom of the dioxygen molecule.[313,314] Other factors also contribute. The increase of effective oxidation state of the metal ion on binding of dioxygen increases the strength of bonds to the other ligands, decreasing their freedom (i.e., results in a further negative entropy contribution). Increased charge separation between the metal ion and the dioxygen ligand increases interaction with polar solvents, another entropically unfavorable process. Because of the fact that coordinate bonds in binuclear dioxygen complexes with peroxo bridges are much more polar than mononuclear "superoxo" dioxygen complexes, the former tend to be formed to a larger extent in water and polar solvents, while 1:1 dioxygen complexes are favored in low dielectric constant solvents.[368,369]

However, the recent work of Nakamoto et al.[368] and Cummings and co-workers[315] seems to contradict some of the earlier assertions. In these recent studies the formation of 1:1 (metal:dioxygen) adducts is favored in polar solvents while 2:1 adducts predominate in less polar solvents. This discrepancy will be discussed in the final portion of this review in light of the available thermodynamic data.

Favorable enthalpy for the dioxygen binding reaction is assisted by increasing the strength of the metal–ligand bonds. The dioxygen ligand receives electron

density from donor atoms in its coordination sphere. Binding of dioxygen is thus a redox process, albeit an incomplete one. An increase in the donor ability of the ligands about the metal ion will increase the electron-donating ability of the metal ion toward dioxygen and would thus be expected to strengthen the $M-O_2$ bond. This phenomenom will be discussed in detail in the following sections.

If the metal–dioxygen bond becomes very strong (i.e., if the electron transfer from metal to dioxygen is essentially complete), the values of K_{O_2} becomes relatively high and reversal of oxygenation becomes an extremely slow process at high pH. Ochiai[90] estimated that oxygenation reactions in which $\Delta G°$ is more negative than -13 kcal mol^{-1} will be irreversible. Technically this conclusion is invalid since the equilibrium, while strongly shifted toward oxygenation, still allows the formation of very low concentrations of dissociated species. A simple calculation of the concentrations of precursor complex and free dioxygen in equilibrium with one of the more stable dioxygen complexes listed in Table IX, at high pH, reveals that the concentration of these species are so low as to be undetectable and hence the conclusion that such systems are irreversible. However, since the ligands coordinated to the metal in these very stable dioxygen complexes are very basic, the degree of dissociation can be increased several orders of magnitude by lowering the pH by only one unit. The reversibility of such dioxygen complexes may thus be readily detected by sufficient lowering of the pH of the solution.

II. Experimental Methods

A. Determination of Equilibrium Constants for Oxygenation

Several methods have been used for determination of oxygenation equilibrium constants, K_{O_2} (eq 13, 14, 19). The choice of method depends to some extent on the magnitude of the equilibrium constant, the type of solvent employed, and the time limitations, as determined by the rate with which the dioxygen complex breaks down to the irreversible species in which the metal becomes permanently oxidized. The equilibrium constants are reported as $1/P_{1/2}$ or $-\log P_{1/2}$ in this review so that comparisons between dioxygen complexes in various solvents, as well as in the solid state, can be made more easily. In the Appendices, the constants are also given in the form in which they were originally reported.

Some of the equilibrium constants reported in the earlier literature were determined by manometric measurements of dioxygen uptake. While this method is certainly valid, it is somewhat inconvenient to use and equilibrium is generally reached rather slowly, so that it has been replaced by other methods. The reader is referred elsewhere for information about this technique.[420] The more commonly employed methods involve spectrophotometric, potentiometric, and polarographic measurements where the equilibrium involved are reached rather quickly and the rate of dioxygen diffusion does not play an important role.

B. Spectrophotometric Determination of Oxygenation Constants

Spectral methods have been almost exclusively employed when organic solvents are used. The method is quite sensitive since the intense charge-transfer band of the dioxygen complex is available as a sensitive probe for the position of equilibrium. Spectral measurements are usually taken under various partial pressures of dioxygen, under conditions such that the dioxygen complex is fully formed at the higher dioxygen concentrations.

For many dioxygen complex systems, such as the cobalt(III) polyamines, the measurements are relatively simple when the absorbance of the precursor complex is very small or negligible compared to that of the dioxygen complex. In other cases such as the cobalt Schiff bases and the cobalt(II) and iron (II) porphyrins, both the oxygenated and unoxygenated forms can have high absorbances. If the complex can be completely oxygenated, so that the extinction coefficient can be determined, the reaction Y of the complex ML that is present as the dioxygen complex MLO_2 may be calculated. This normally requires measuring absorbances at several different wavelengths corresponding to each of the species present in solution. Simple computational methods can be applied to give each of the individual concentrations, although only the $[MLO_2]$ is needed since $[ML]_T$ is fixed for the experiment (eq 23 and 24). Usually the spectra are not well-behaved (i.e.,

$$A_T{}^{\lambda}j = \sum_{i}^{n} \epsilon_i C_i \quad \text{for } j = 1 \text{ to } n \tag{23}$$

$$Y = [MLO_2]/[ML]_T \tag{24}$$

no individual absorption bands for ML and MLO_2). In this instance the problem is simplified by assuming that only the complexes contribute to the total absorbance. Together with the mass balance equation an expression for Y can be written (eq 25 and 26) (A_0) is the initial

$$[ML]_T = [ML] + [MLO_2] \tag{25}$$

$$Y = \frac{(A_T - A_0)/(\epsilon_{MLO_2} - \epsilon_{ML})}{[ML]_T} \tag{26}$$

absorbance corresponding to ML). The equilibrium constant K_{O_2} may be obtained directly from a plot of $\log (Y/(1 - Y))$ against $\log P_{O_2}$ and the value of P_{O_2} selected under the conditions such that $Y = 1 - Y$:

$$K_{eq} = \frac{[LCoP_{O_2}]}{[LCoP]P_{O_2}} = \frac{Y}{(1 - Y)P_{O_2}} \tag{27}$$

Many complex systems do not achieve 100% oxygenation even under excessive dioxygen pressure. In these cases extrapolation to infinite pressure gives A_∞ from which ϵ_{MLO_2} may be obtained. Many workers vary A_∞ until a best fit of eq 27 results. Another method used by Drago[422] and others[500] treats both ϵ_{MLO_2} and K_{O_2} as unknowns. Substituting the appropriate mass balance equations for $[ML]_T$ (eq 25) and $[O_2]_T$ (eq 28) into

$$[O_2]_T = [O_2] + [MLO_2] \tag{28}$$

the equilibrium expression defining K_{O_2} (eq 15) and writing the total absorbance as a function of $[ML]_T$ and

$[MLO_2]$ (eq 29) gives an expression (eq 30) which has

$$[MLO_2] = (A_T - A_0)/(\epsilon_{MLO_2} - \epsilon_{ML}) \quad (29)$$

$$K_{O_2}^{-1} = \frac{A_T - A_0}{\epsilon_{MLO_2} - \epsilon_{ML}} - [ML]_T - [O_2]_T + \frac{[ML]_T[O_2](\epsilon_{MLO_2} - \epsilon_{ML})}{A_T - A_0} \quad (30)$$

two unknowns, ϵ_{MLO_2} and K_{O_2}. For a series of experimental conditions a set of simultaneous equations is generated which can be solved by suitable least-squares analysis to give best-fit values of ϵ_{MLO_2} and K_{O_2}.

The major problem encountered in applying the spectrophotometric method is interference from other complex equilibria. Porphyrin complexes, for example, can add 2 equiv of a basic ligand in axial positions, as follows:

$$MP + L \rightleftharpoons LMP \quad (31)$$

$$LMP + L \rightleftharpoons LMPL \quad (32)$$

The oxygenation reaction then involves competition with the second mole of the axial ligand. Since some of the secondary ligand is needed to form the dioxygen complex $LMPO_2$, its concentration in solution must be maintained at a sufficiently high level to produce a considerable concentration of LMP without driving the equilibrium completely toward the fully coordinated form, LMPL. It is seen that competitive reactions of this type may thus complicate the calculations as well as the spectra.

$$LMPL + O_2 \rightleftharpoons LMPO_2 + L \quad (33)$$

While the relationships given above appear straightforward, the application of this "limiting spectra" approach to real systems has been subject to some question. Some of the problems have been discussed by Ibers et al.,[421] Guidry and Drago,[422] and Basolo et al.[423] No attempt is made in this review to resolve the issues involved, but interested readers are referred to the appropriate literature. The data published by various workers are assumed to be valid, and all available equilibrium data are included in the tables at the end of this paper.[424-429]

C. Potentiometric Methods

While the "limiting spectra" method may be applied in aqueous as well as organic media, potentiometric measurements of hydrogen ion concentration normally gives more accurate equilibrium data and involves fewer experimental difficulties. This method involves measurement of hydrogen ion concentration during the addition of increments of base to a solution containing the acid form of the ligand and the metal ion in the presence of dioxygen at a controlled value of the ionic strength. It is essential that carbon dioxide be excluded from the reaction vessel and that sufficient time be allowed for equilibration after each addition of base. Interpretation of the data obtained requires an independent determination of the ligand protonation constants and the equilibrium constant(s) for formation of the metal–ligand complex(es). These values may be obtained easily by similar potentiometric measurements of solutions of the ligand and of stoichiometric mixtures of the ligand and the metal ion, respectively, under an inert, dioxygen-free atmosphere.

Calculation of the value of K_{O_2} from the potentiometric data may be carried out by solution of the pertinent equilibrium and mass balance relationships for each experimental point in the buffer region(s) in which dioxygen complex formation occurs. The precise relationships employed depend upon the nature of the ligand(s) and metal ion involved. The example given below (eq 34–37)[430] involves oxygenation of cobalt complexes of pentadentate ligands having five dissociable protons (H_2L), where T_L represents the total

$$T_L = A_1[L] + X_1[ML] + 2[M_2L_2O_2] \quad (34)$$

$$T_M = Y_1[M] + X_1[ML] + 2[M_2L_2O_2] \quad (35)$$

$$B = T_B + [H^+] = [OH^-] = A_2[L] + X_2[ML] + Y_2[M] + 10[M_2L_2O_2] \quad (36)$$

$$K_{O_2} = \frac{[M_2L_2O_2]}{[M]^2[L]^2[O_2]} \quad (37)$$

analytical ligand concentration, T_M the total analytical metal ion concentration, and B the total analytical concentration of hydrogen ions which are initially bound to the ligand, T_B represents the total analytical concentration of base added, and the hydroxide ion concentration term corrects B for hydrogen ion formed by the dissociation of water. The remaining terms are defined in eq 38–46. Suitable computer programs have been devised for determining the best value of K_{O_2} from these relationships and the measured potentiometric data.[431]

$$A_1 = 1 + K_1^H[H^+] + K_1^HK_2^H[H^+]^2 + ... + K_1^HK_2^HK_3^HK_4^HK_5^H[H^+]^5 \quad (38)$$

$$A_2 = 5 + 4K_1^H[H^+] + 3K_1^HK_2^H[H^+]^2 + ... + K_1^HK_2^HK_3^HK_4^H[H^+]^4 \quad (39)$$

$$X_1 = 1 + K_{MHL}^H[H^+] \quad (40)$$

$$X_2 = 5 + 4K_{MHL}^H[H^+] \quad (41)$$

$$Y_1 = (1 + K_{MOH})/[H^+] \quad (42)$$

$$Y_2 = K_{MOH}/[H^+] \quad (43)$$

$$K_i^H = \frac{[H_nL^{n+}]}{[H^+][H_{n-1}L^{(n-1)+}]} \text{ for } i = 1 \text{ to } 5;\ n = 5 \text{ to } 1 \quad (44)$$

$$K_{MHL}^H = \frac{[MHL]}{[ML][H^+]} \quad (45)$$

$$K_{MOH} = \frac{[MOH^{1+}][H^+]}{[M^{2+}]} \quad (46)$$

The major drawbacks of the potentiometric method are (1) that it is not readily applied in nonaqueous solutions since the essential standard electrode potentials are not generally available and (2) the method is unsuitable for dioxygen complexes (e.g., iron–dioxygen

complexes) that readily form μ-oxo dimers in aqueous solution and mixed solvents in which water is a significant component. In practice, the technique has been used mainly with binuclear Co(II)–dioxygen complexes in aqueous solution. It should be noted that formation of a μ-hydroxo bridge in addition to the μ-peroxo bridge normally formed on reaction of Co(II) complexes with dioxygen will release an additional half mole of hydrogen ion per mole of cobalt–dioxygen complex formed and the expressions for B (eq 36) and K_{O_2} (eq 37) must be altered accordingly.

A technique which is often used to obtain oxygenation equilibrium data for compounds which rapidly decompose to irreversibly oxidized Co(III) species is based on polarographic determination of dioxygen concentration at equilibrium. As with the potentiometric method, interpretation of the data requires knowledge of the ligand protonation and chelate formation constants. The stoichiometry of the oxygenation reaction must also be determined. Oxygenation constants obtained by this technique have been shown to be comparable to those obtained potentiometrically.[355]

The experimental technique usually employed involved the measurement of free oxygen concentration before and after addition of the metal complex with which it combines, and the amount of oxygen which has reacted may then be calculated. Calculation of the oxygenation equilibrium constant requires the solution of four equations (47–50) for each measurement. Data are generally taken at several pH values to insure that the K_{O_2} values are constant over the pH range of the reaction of the dioxygen complex. The symbols em-

$$T_L = A_1[L] + X_1[ML] + 2[M_2L_2O_2] \quad (47)$$

$$T_M = Y_1[M] + X_1[ML] + 2[M_2L_2O_2] \quad (48)$$

$$[ML] = K_{ML}[M][L] \quad (49)$$

$$[M_2L_2O_2] = (2.75 \times 10^{-4})(1 - \sigma) \quad (50)$$

ployed have been defined previously (38–43), except for σ, which is the fractional oxygen saturation of the solution after equilibrium is reached. The molar concentration of oxygen in air-saturated 0.100 M KNO_3 solution at 25 °C is 2.75×10^{-4}. Other values are available for other temperatures or ionic strengths.

D. Free Energies, Enthalpies, and Entropies of Oxygenation

Values of $\Delta G°_{O_2}$ may be obtained from K_{O_2} values by using the relationship

$$\Delta G°_{O_2} = -RT \ln K_{O_2} \quad (51)$$

The thermodynamic parameters $\Delta H°$ and $\Delta S°$ are determined either by calorimetric methods or from the temperature dependence of K_{O_2}. An excellent review of the application of thermochemistry (e.g., calorimetry) to bioinorganic systems is now available.[432]

The calorimetric approach allows the value of $\Delta H°$ to be measured directly. Since metal chelate formation and oxygenation in solution are frequently simultaneous or overlapping reactions, it is generally necessary to determine the enthalpies of these two processes independently. If titration calorimetry is employed and the dioxygen concentration is determined continuously during the titration (by means of a polarographic O_2 probe, for example), these contributions may be determined with the aid of known values of the corresponding equilibrium constants. If the dioxygen complex is essentially fully formed in the presence of any amount of ML complex, a separate measurement of the enthalpy of chelate formation must be made under a dioxygen-free atmosphere. Measurements under a dioxygen atmosphere will then give an enthalpy which is the sum of the enthalpies of chelate formation and of oxygenation.

The value of $\Delta H°$ may also be obtained by evaluating the temperature dependence of the equilibrium constant K_{O_2} (eq 52). A plot of $\ln K_{O_2}$ against $1/T$ (termed a Van't Hoff plot) should give a straight line with a slope equal to $-\Delta H°/R$.

$$\frac{d \ln K_{O_2}}{d(1/T)} = \frac{-\Delta H°}{R} \quad (52)$$

Once $\Delta H°$ values have been determined by either method, $\Delta S°$ may be determined from the usual relationship (eq 53). The enthalpy and entropy changes

$$\Delta G° = \Delta H° - T\Delta S° \quad (53)$$

that have been determined for the oxygenation of complexes are presented in Appendices I and II and will be considered in some detail in the discussion of the factors that influence the strength of metal–dioxygen bonding.

E. Solid-State Equilibria

Some equilibrium constants have been measured[93,116,120,433] for the oxygenation of solid complexes (Appendix I). Special care must be taken in interpretating the results of such studies.[82] For example, a compound which does not react with molecular oxygen in the solid state may have the potential to form a dioxygen complex and yet be prevented from doing so by the nature of the packing of metal complex molecules in the crystalline state. Binding of dioxygen at measurable rates by solid-state complexes requires a crystal lattice with sufficiently large holes to allow dioxygen to diffuse rapidly throughout the solid.[82] An arrangement of molecules favorable to dioxygen bridging between adjacent complexes is also required for those compounds for which bridging is essential to dioxygen binding.[82] It is also essential that processes other than those in a simple three-phase system (metal chelate, O_2(g), and dioxygen complex) be recognized. Calvin and co-workers, for example, noted that the unoxygenated phase of various cobalt salicylideneamine complexes disappears completely at 75% oxygenation and that a solid solution is formed.

A more recent example of a solid-state synthetic oxygen carrier that undergoes oxygenation without a phase change is the 2-methylimidazole–picket-fence iron(II) complex reported by Jameson et al.[179] Apparently, crystallinity is maintained during oxygenation. Because of the space available in the crystal lattice, and particularly at the oxygenation site, reaction with dioxygen results in only minor changes in intermolecular spacing. Thus the crystal structure does not significantly change during oxygenation, so that the solid–gas

equilibrium is expressed by the relationship

$$X/(1 - X) = KP_{O_2} = P_{O_2}/P_{1/2}$$

where X = mole fraction of oxygenation sites and $1 - X$ = mole fraction of unoxygenated sites. Accordingly, the oxygenation of the iron(II) picket-fence complex as a function of increasing dioxygen pressure follows a sigmoidal curve characteristic of a solid solution, rather than a transition at constant dioxygen pressure characteristic of the formation of a new solid phase. The relatively minor changes in crystal dimensions result in a minor increase in K as the degree of oxygenation increases, a phenomenon that has been compared to cooperativity in hemoglobin oxygenation.[36,314] However, in this case the increase is probably due to the small changes in molecular dimensions of the complex on oxygenation, which slightly inhibits the oxygenation process when a dioxygen complex is surrounded by unoxygenated complex molecules and is constrained to the dimentions of the unoxygenated crystal structure. With a high degree of oxygenation, however, the crystal dimensions have been sufficiently modified to remove these constraints, allowing for a better fit of the newly oxygenated complexes in the crystal lattice.

Assuming that the problems involved in attaining equilibrium throughout the solid phase(s) can be overcome, the solid-state equilibrium can be measured by determining the dioxygen uptake at equilibrium as a function of its partial pressure over the solid; the treatment is essentially the same as that for solutions discussed previously. Any physical measurements which distinguish between the oxygenated and unoxygenated species (e.g., reflectance spectra, complex weight, magnetic susceptibility, etc.) may be obtained calorimetrically or by varying the temperature at which equilibrium measurements are performed.

III. Properties of Dioxygen Complexes

A. Major Classes

It is instructive to divide naturally occurring dioxygen complexes into two classes on the basis of function. *Oxygen carriers* mediate the transport of dioxygen within or between tissues. *Reactive dioxygen complex intermediates* are formed in processes which ultimately result in the biological reduction of dioxygen, superoxide, or peroxide. Such processes are usually accompanied by oxidation of an organic substrate to form a product which is useful to the organism or must be disposed of. The major difference between these classes of compounds is the ultimate fate of the dioxygen ligand.

Oxygenation of an oxygen carrier must be reversible in order that dioxygen may be released unchanged in tissues where dioxygen tension is low. It follows that reduction of dioxygen and oxidation of the metal ion to which it is attached must be partial. Many of the unique chemical features of the oxygen carriers are required to insure that the redox process will be partial. The reactive intermediate, on the other hand, must release dioxygen in a reduced form; the redox process must be completed in this case. Naturally, the thermodynamic properties required for a complete redox process differ from those required for a reversible partial redox process. It follows that the division of dioxygen complexes into two classes has a thermodynamic as well as a functional basis. In this regard it is interesting to note that no dioxygen complex is known to be employed in both dioxygen transport and dioxygen activation in biological systems.

Thermodynamic data reported in the literature in most cases involve systems that undergo reversible oxygenation.[434-502] This is due in part to the greater ease of working with these systems. Unfortunately, the more stable, less reversible systems are often ignored because they are poor models for oxygen carriers. One can argue, however, that it is less important to understand the oxygen carriers than it is to understand the dioxygen complexes which serve as reactive intermediates. While the former have few applications outside of biological systems, the latter are potentially important catalytic intermediates in processes which participate in a greater variety of biological reactions than do the oxygen carriers. It must be stressed, then, that the so-called "*irreversible*" systems are more likely than the easily "reversible" systems to yield information about dioxygen complexes as reactive intermediates.

B. Naturally Occurring Oxygen Carriers

The major biological oxygen carriers are conveniently classified into three groups: hemoglobins,[4,20,24] hemerythrins,[22] and hemocyanins.[23] Myoglobins, erythrocruorins, and chlorocruorins are related to hemoglobins. Hemovanadin,[9,14] if it actually serves a respiratory function, must be considered to be of minor importance due to its limited biological distribution.[503] A summary of oxygen carrier properties is given in Table I.

Hemoglobin (Hb) is the major respiratory protein in higher vertebrates, notably man. Because of its biochemical and medical significance, the extensive variety of techniques which may be employed in its study, and the relative ease with which it may be isolated and purified, hemoglobin has probably been studied more extensively than any other protein. Hemoglobin has a quaternary structure resulting from the interaction of the four subunits, two α chains and two β chains. The β chains are somewhat larger than the α chains (146 amino acid residues for the β chain vs. 141 residues for the α chain in horse hemoglobin[4]). Each chain forms a tertiary structure having a pocket in which a heme group is bound through van der Waals contacts, hydrogen bonding, and a coordinate bond to the imidazole group of a histidine residue. This heme group is accessible to and coordinates small neutral molecules such as dioxygen and carbon monoxide and anions such as fluoride, chloride, hydroxide, and cyanide. The structure of hemoglobin is illustrated in Figure 7.

It is of interest to note that subunits are not necessarily of constant composition.[504] Apparently all vertebrates contain multiple hemoglobins.[505] This phenomenon is related to changes in the respiratory requirements during particular periods of development. Human hemoglobin during fetal development, when dioxygen must be obtained from the mother's hemoglobin, contains α chains associated with high affinity ϵ chains. Later in pregnancy these ϵ chains are replaced by γ chains. Normal adult blood contains mostly hemoglobin A with a small amount of hemoglobin A_2 which consists of δ chains in place of α chains.

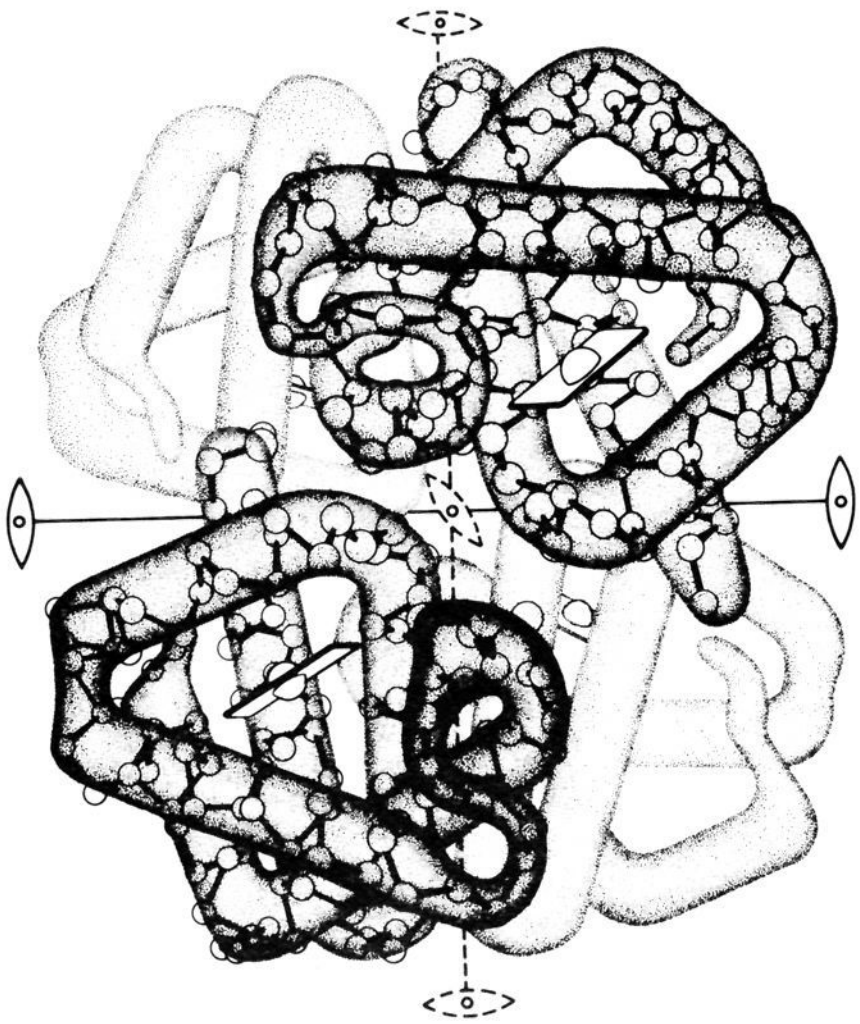


Figure 7. Illustration of the quaternary structure of hemoglobin. Adapted from ref 507. Reprinted with permission from: Dickerson, R. E.; Geis, I. "The Structure and Action of Proteins"; Benjamin/Cummings, 1969. Copyright 1969, Dickerson and Geis.

The function of the protein is somewhat complicated owing to interaction between subunits which affect the dioxygen binding properties of the heme prosthetic groups. These factors will be discussed below.

1. *Myoglobin*

It will be instructive to first consider myoglobin (Mb), a protein composed of a single chain of 153 amino acid[506] containing only one prosthetic group binding site per protein molecule. Myoglobin bears a striking similarity to an isolated hemoglobin subunit both in structure and in dioxygen affinity. Figure 8 illustrates the structure of the protein. The tertiary structure includes a "pocket" or "cleft" containing a heme group (heme is a planar four-coordinate iron(II) protoporphyrin complex).[507] The imidazole nitrogen of the histidyl residue F8 (the proximal imidazole) provides a fifth coordinated donor group. The ferrous ion is thus pentacoordinate. Structural studies on hemoglobin and myoglobin have revealed that the ferrous ion is displaced approximately 0.3–0.6 Å out of the porphyrin plane toward the proximal imidazole.[5,100,508] In this configuration, the metal ion is somewhat protected from interactions with the solvent. Small molecules such as dioxygen, however, can readily enter the distal pocket and bind to the metal ion at the sixth coordinate site to form an octahedral complex. Case and Karplus[509] have considered the dynamics of oxygen binding to myoglobin with a theoretical model consisting of both adiabatic and diabatic limits. The distal histidine (HIS-E7) and valine (VAL-E11) residues serve to protect the dioxygen binding region. Hydrogen bonding between the imidazole group of HIS-E7 and the dioxygen ligand has been discussed previously. Horse

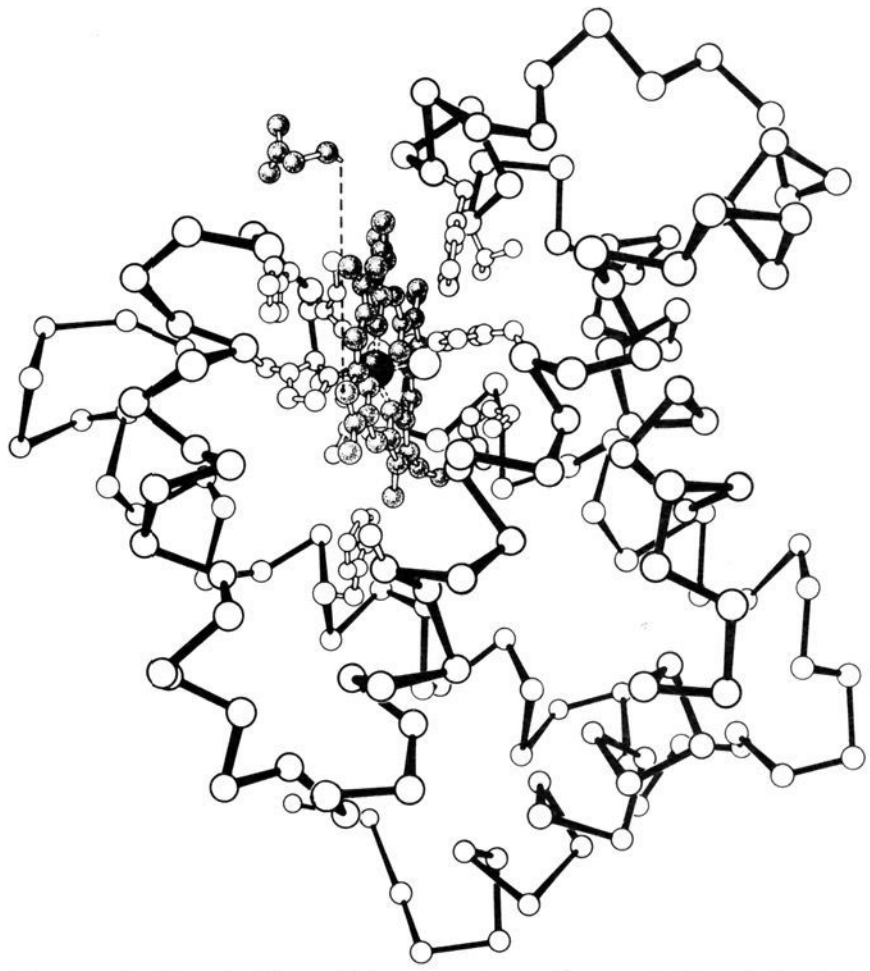


Figure 8. Illustration of the structure of myoglobin. Adapted from ref 507. Reprinted with permission from: Dickerson, R. E.; Geis, I. "The Structure and Action of Proteins"; Benjamin/Cummings, 1969. Copyright 1969, Dickerson and Geis.

heart myoglobin will be half saturated with dioxygen at 1 torr in 0.10 M TRIS buffer[510] or at 0.50 torr in 0.10 M phosphate buffer[511] ($P_{1/2}^{-1}$ = 1.4 × 10^3 and 7.38 × 10^2 atm^{-1}, respectively). Comparable values of $P_{1/2}^{-1}$ for isolated α and β chains in 0.10 M phosphate buffer are 1.2–1.3 × 10^3 and 2.6–3.2 × 10^3 atm^{-1}, respectively.[512,513] Oxygenation of myoglobin is easily and completely reversible.

The controversy concerning the oxidation state of iron in oxygen carriers was previously discussed. Oxymyoglobin is best considered to be an iron(III) complex containing uninegatively charged dioxygen.[100,153] The coordination sphere of this low-spin formally Fe^{III}-O_2(−I,0) system conforms closely to octahedral geometry. To achieve this geometry, the ferric ion moves toward the plane of the porphyrin ring. The proximal histidine moves with the metal ion to which it is attached. The magnitude of this movement by the iron has come under question recently because of reports of a high-spin iron(II) porphyrin where the iron resides strictly in the plane of the porphyrin[514] and a low-spin iron(III) porphyrin which has only a small (~0.3 Å) displacement of the iron from the porphyrin plane.[515]

Myoglobin is a storage rather than a transport protein. It is found in the muscle tissues of vertebrates and invertebrates[516] to which it imparts a dark color. The major concentration in man occurs in cardiac muscle,[516] where an anoxic condition (ischemia) can be life threatening. To function properly as a dioxygen storage site, myoglobin must be able to accept dioxygen from hemoglobin and release it to anoxic tissues. It must therefore have a dioxygen affinity high enough to remove dioxygen from hemoglobin but low enough to allow eventual release to the tissues. Comparison of the dioxygen affinities in Appendix II reveals that, even in the absence of allosteric modifiers of hemoglobin such

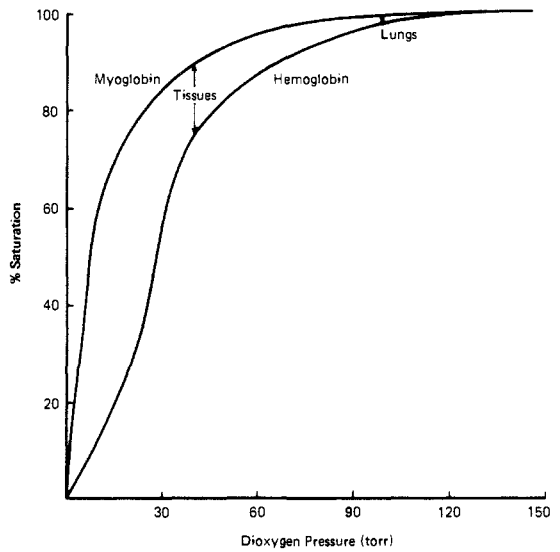


Figure 9. Dioxygen saturation curves for myoglobin and hemoglobin at pH 7.4 and 25 °C.

as phosphate and 2,3-diphosphoglycerate (2,3-DPG), the dioxygen affinity of myoglobin is greater than that of hemoglobin. Myoglobin can be considered a dioxygen transport protein only in the limited sense that it facilitates (increases the rate of) dioxygen diffusion into muscle tissue.[517-520] This is, however, an important function and a shortage of myoglobin (myoglobinemia) can have pathological consequences.[521]

2. Hemoglobin

Cooperative Effects. Figure 9 is a plot of percentage dioxygen saturation against dioxygen partial pressure for myoglobin and hemoglobin. There is a striking difference in the shapes of the saturation curves. Myoglobin exhibits a hyperbolic curve characteristic of systems where the binding sites are independent of one another. Hemoglobin exhibits a sigmoidal curve characteristic of systems where the binding sites are not independent. Because of the extreme similarity (both in structure and in dioxygen affinity) of the individual hemoglobin subunits to the myoglobin molecule, one must conclude that the differences in the saturation curves should be attributed to subunit interaction in the hemoglobin molecule. These interactions are collectively termed cooperative interactions. The subunits in hemoglobin initially influence one another so as to achieve a lower dioxygen affinity. Binding of dioxygen at some sites decreases this influence, effectively increasing the dioxygen affinity of the remaining sites. Hemoglobin thus requires a much smaller change in P_{O_2} to effect loading or unloading of dioxygen compared with myoglobin. In addition to these cooperative effects which decrease the dioxygen affinity for the hemoglobin molecule there are functional differences in the α and β chains which also contribute to many of the properties of the protein (ref 235, 522-524).

It is useful to have a quantitative measure of cooperativity in proteins. This indication of subunit interaction is provided by the Hill coefficient, n.[525] Hill coefficients for some naturally occurring oxygen carriers are summarized in Table X. These values are also provided in Appendix I whenever available. The Hill

TABLE X. Representative Values of the Hill Coefficient in Natural Oxygen Carriers

protein	conditions	n	ref
human HbA	pH 7.4 (BIS-TRIS buffer), 25 °C	2.51	434
	pH 7.1 (phosphate buffer), 25 °C	2.75	436
	pH 7.4 (BIS-TRIS), 25 °C, 2 mM, 2,3-DPG	3.09	434
earthworm Hb	pH 7.4 (phosphate), 20-21 °C	4	511
ghost shrimp[a] Hcy C	pH 7.65 (TRIS), 25 °C	1.28	469
shrimp[b] Hcy	pH 7.60 (TRIS), 20 °C, 10 mM $CaCl_2$	4.0	468
Spirographus[c] ChL	pH 7.5 (TRIS), 20 °C	3.2	466

[a] *Callianassa californicnsis.* [b] *Penacus setiferus.* [c] *Spirographus spallanzanii.*

equation relates the fractional dioxygen saturation (y) of the protein to either the dioxygen partial pressure[526] (eq 54) or the dioxygen activity, X (eq 55).[527] In the

$$\log (y/1 - y) = n \log P_{O_2} - n \log P_{1/2} \quad (54)$$

$$\ln (y/1 - y) = n \ln X - n \ln X_{1/2} \quad (55)$$

absence of subunit interactions, a plot of log $(y/1 - y)$ against log P_{O_2} will yield a straight line with a slope of unity (i.e., $n = 1$). Thus the Hill coefficient is generally not constant except for simple single-site systems but varies with the degree of saturation y.

To demonstrate the viability of the Hill equation, two cases may be considered. The first is oxygenation of a protein having n independent dioxygen binding sites. A general expression for fractional saturation based on simple mass balance relationships and equilibrium constants is given in eq 56. This mathematical rela-

$$\bar{\nu} = \frac{\sum_{i=1}^{n} i K_{O_2}{}^i P_{O_2}{}^i}{1 + \sum_{i=1}^{n} K_{O_2}{}^i P_{O_2}{}^i} \quad (56)$$

tionship is sometimes referred to as the Adair equation with n binding sites, each of which has an intrinsic binding constant K. These intrinsic constants however are not equal if the sites are identical since there is a statistical factor involved. The Adair equation may be rewritten (eq 57) as indicated. Application of the binomial expansion gives eq 58. The index in the latter

$$\bar{\nu} = \frac{\sum_{i=1}^{n} i \frac{n!}{(n-1)!i!} K_{O_2}{}^i P_{O_2}{}^i}{1 + \sum_{i=1}^{n} \frac{n!}{(n-1-i)!i!} K O_2{}^i P_{O_2}{}^i} \quad (57)$$

$$(1 + K_{O_2} P_{O_2})^{n-1} = \sum_{i=1}^{n-1} \frac{(n-1)!}{(n-1-i)!i!} K_{O_2}{}^i P_{O_2}{}^i = \frac{1}{n K_{O_2} P_{O_2}} \sum_{j=1}^{n} j \frac{n!}{(n-j)!j!} K_{O_2}{}^j P_{O_2}{}^j \quad (58)$$

equation has been changed ($j = i + 1$) so that the initial expression may reduce to a more convenient form (eq 59). Rearranging this equation using the definition of

$$\bar{\nu} = \frac{nK_{O_2}P_{O_2}(1 + K_{O_2}P_{O_2})^{n-1}}{(1 + K_{O_2}P_{O_2})^n} = \frac{nK_{O_2}P_{O_2}}{1 + K_{O_2}P_{O_2}} \quad (59)$$

$P_{1/2} = (K_{O_2})^{-1}$ (eq 17) and $y = \bar{\nu}/n$ (where y is the number of sites bound per total macromolecule) and then taking the logarithm of both sides generate the familiar Hill equation (eq 54). It is important to note that n is equal to unity for a protein containing any number of independent and identical binding sites.

The second case is a multisite protein in which all the sites oxygenate simultaneously (i.e., infinite interaction between sites). Only the last term in the numerator and the first and last terms in the demoninator of eq 56 are important. This will then reduce to eq 60 directly. Again, if the substitutions $y = \bar{\nu}/n$ and $P_{1/2}{}^n = (K_{O_2})^{-n}$ are made, this equation may be rearranged to give, upon taking logarithms, eq 54.

$$\bar{\nu} = \frac{nK_{O_2}P_{O_2}{}^n}{1 + K_{O_2}P_{O_2}{}^n} \quad (60)$$

In the real systems where multiple binding sites exist, infinite site–site interaction is not possible. In such cases, the slope of the Hill plot (n) will asymptotically approach unity at very low and very high fractional saturations (Figure 10). At very low fractional saturation the protein exhibits behavior characteristic of n independent binding sites while at the other extreme only one binding site is available. Equilibrium constants for these first and last steps may be obtained. Determining the intermediate equilibrium constant is not quite so simple. In addition, the Hill constant n will never attain its maximum value (i.e., no protein has infinite site–site interactions). As such the appropriate equations become more complicated under real conditions. The expression for fractional dioxygen saturation of hemoglobin, for example, must include both fully and partially oxygenated species. The simple expressions for K_{O_2} are replaced by an expression which requires knowledge of equilibrium constants for addition of each dioxygen ligand (often called Adair constants).

$$y = \frac{\sum_{a=1}^{4} a[\mathrm{Hb}(O_2)_a]}{4\sum_{a=0}^{4}[\mathrm{Hb}(O_2)_a]} \quad (61)$$

Detailed mathematical models for the interactions between dioxygen binding sites have been proposed.[4,26,527-259] The most widely accepted model is the Monod–Wyman–Changeux (MWC) model,[4,527] which does not distinguish between α and β subunits. The protein is postulated to exist in R (relaxed) and T (tense) states, each conformation having a set of stepwise equilibria of the form indicated by eq 62 and 63, where n = 1–4 for hemoglobin. The dioxygen affinities

$$\mathrm{R}(O_2)_{n-1} + O_2 \overset{K_{R_n}}{\rightleftharpoons} \mathrm{R}(O_2)_n \quad (62)$$

for the two states are different. The dioxygen dissociation curve or the Hill plot can be calculated from a knowledge of the number of binding sites (n), the equilibrium constant for the equilibrium between unligated R and T states (L_0, eq 64) and the constant ratio between equilibrium constants for binding by R and T states (α, eq 65).[527] Cooperativity occurs in this model

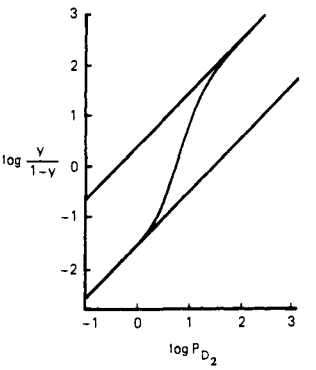


Figure 10. Hill plot of the dioxygen equilibrium of hemoglobin at pH 7 and 25 °C, where y is the fraction of sites oxygenated. P_{O_2} is the dioxygen pressure on torr. Adapted from ref 4.

$$\mathrm{T}(O_2)_{n-1} + O_2 \overset{K_{T_n}}{\rightleftharpoons} \mathrm{T}(O_2)_n \quad (63)$$

$$\mathrm{R}_0 \overset{L_0}{\rightleftharpoons} \mathrm{T}_0 \qquad L_0 = [\mathrm{T}_0]/[\mathrm{R}_0] \quad (64)$$

$$\alpha = K_{R_n}/K_{T_n} \quad (65)$$

because, while deoxygenated hemoglobin exists mainly in the T form (L_0 is high), dioxygen binds more readily to the R form. Binding of dioxygen removes R_0 and shifts the equilibrium in eq 64 to the left.[4]

The Koshland–Nemethy–Filmer (KNF) model also ignores the difference between α and β subunits. It postulates that oxygenation of any subunit affects the affinity of its nearest neighbor for dioxygen. The cooperativity depends on this interaction. The important parameter is an interaction parameter, U. When $U >$ 1, the interaction is cooperative. The problem is stated in terms of a partition coefficient which partitions the dioxygen among the various possible states according to their probability of occurrence.[4] The statistical mechanical model of Stanely, Bansil, and Herzfeld[25] is similar to the KNF model. The intermediate compound model proposed by Adair,[530-535] which provides a different intrinsic binding constant for hemoglobin and for each of the partially oxygenated species of hemoglobin, is of course able to formally correlate with cooperativity.

A detailed analysis of these mathematical models is not justified at this point. The MWC model fits most of the early data on hemoglobin. This success and the support of the structural work of Perutz et al.[5,228-230,232-234] gave the model wide recognition. The Perutz model evolved from the gross changes in the $\alpha\beta$ interfaces as seen in structural studies on deoxyhemoglobin and methemoglobin. A fundamental postulate of this model is that the movement of the heme iron into the plane of the porphyrin ring upon oxygenation (due to a change in ionic radius and spin state) pulls the proximal imidazole along with it, and in turn triggers major conformational changes leading to increased affinity for dioxygen. This model received support from Szabo and Karplus[536] with a statistical thermodynamic model for correlating structural changes which accompany oxygenation and protonation by hemoglobin with the known solution properties.

More recently the Perutz model has received critical tests.[509,537-541] Extended X-ray absorption fine structure (EXAFS) studies[508] have shown that the displacement

TABLE XI. Adair Constants for Oxygenation of Sheep Hemoglobin[a,b]

constant	K_1	K_2	K_3	K_4
K_i,[c] torr^{-1}	0.002	0.196	0.149	2.00
k_i(rel)	1	1.76	1.31	17.7
K_i(predicted)	1	0.376	0.167	0.0625
K_i(rel)/K_i(predicted)	1	4.7	7.9	283

[a] From ref 529. [b] Constants obtained at 19 °C, pH 9.1. [c] K_i is the equilibrium constant for the ith equilibrium step, $Hb(O_2)_{i-1} + O_2$ (K_i) $Hb(O_2)_i$.

of the heme iron upon oxygenation is much less than previously thought.[542] A thermodynamic analysis by Johnson and Ackers[543] which is based on the Szabo–Karplus model but includes the properties of dissociated dimers in equilibrium with tetramers argues against the Perutz mechanism. Additional work from Pettrigrew et al.[544] on 22 mutant and chemically modified hemoglobins suggests that cooperativity in dioxygen binding is a reflection of the protein–protein interactions within the $\alpha_1\beta_2$, $\alpha_2\beta_1$, and $\alpha_1\alpha_2$ contact region. Apparently the movement of the heme iron is not the primary "trigger" for cooperativity as outlined by Perutz. Small subtle changes throughout the molecule result in the observed differences in dioxygen affinity. Warshel and Weiss[545] view cooperativity as two opposing interactions. R state interactions stabilize the transfer of positive charge to the porphyrin system by permanent and induced protein dipoles. The T state, however, has stronger interactions with neighboring subunit charges and dipoles. The observed 3.6 kcal/mol heme–heme interaction energy results from competition between these forces.

It is instructive to consider the extent to which cooperativity increases the dioxygen affinity of a partially oxygenated hemoglobin molecule. According to the analysis of Ochiai,[546] the final Adair constant is 283 times the value which is predicted in the absence of cooperative interactions (Table XI). Furthermore, the dioxygen affinity increases monotonically with the extent of oxygenation.

The Hill plot can yield other information in addition to the value of n, which is the maximum slope of the plot. As mentioned previously, extension of the upper and lower positions of the curve in Figure 10 to the x axis yields $P_{1/2}$ values for the R and T states of the MWC model or of the highest and lowest affinity states in a multistate model. Furthermore, the total free energy of interaction (the free energy difference between R and T states) is proportional to the horizontal distance between the assymptotes ($\Delta \ln X$), and the interaction free energy at any degree of saturation may be determined from eq 67.[527] Note that the free energy of interaction does not go to infinity if the site–site interaction is infinite.

$$\Delta G^\circ_I = -RT\Delta \ln X \tag{66}$$

$$\Delta G^\circ_I = \left(\frac{RT}{y(1-y)}\right)\left(1 - \frac{1}{n}\right) \tag{67}$$

Allosteric Modification. Cooperativity is the result of allosteric modification of hemoglobin. Because the modification is caused by the same ligand species as that whose binding is affected, it is termed homotropic.[528] The binding of dioxygen is also affected by a number of heterotropic modifications, including those brought about by H^+ (Bohr effect), CO_2, and organic phosphate.[547] These allosteric modifiers are responsible for the low dioxygen affinity of hemoglobin under physiological conditions ($P_{1/2} \approx 26$ torr) when compared with the "stripped" protein ($P_{1/2} \approx 5$ torr).

TABLE XII. Subunit Salt Bridges and Hydrogen Bonds[a,b]

intrasubunit interactions	intersubunit interactions
TYR-140α - - -VAL-93α	T structure
TYR-145β - - -VAL-98β	LYS-127α_1 · · · ARG-141α_2
HIS-146β · · · ASP-94β	ARG-141α_2 · · · ASP-126α_1
VAL-1β · · · O-PO_3^{2-}	LYS-40α_1 · · · > HIS-146β_2
LYS-82β	VAL-1β · · · /
	LYS-82 · · · - \
	HIS-2 · · · · · — 2,3-DPG
	HIS-143 · · - /
	TYR-42α_1 - - -ASP-99β_2
	R structure
	LYS-127α_1 · · · ARG-141α_2
	VAL-1β_1 · · · HIS-146β_2
	ASP-94α_1 · · · ASP-102β_2

[a] Adapted from Perutz, M. F.; Ladner, J. E.; Simon, S. R.; Ho, C. *Biochemistry* 1974, *13*, 2163. [b] Salt bridge (· · ·); hydrogen bonding (- - -).

The Bohr effect (after Danish physiologist Christian Bohr) is a decrease in the dioxygen affinity of hemoglobin under conditions of increased acidity. Tissues undergoing respiration give off carbon dioxide which is converted to H^+ and HCO_3^- by the enzyme carbonic anhydrase.[548,549] These tissues have an environment which is more acidic than the site of dioxygen uptake (i.e., the lungs). The Bohr effect thus helps insure that dioxygen will be released to those tissues which have the greatest oxygen requirement. The effect is due to structural changes which occur in the molecule upon oxygenation. These structural changes cause a decrease in the effective basicity of certain basic amino acid side-chain groups.[550] An increase in the proton concentration favors the more basic deoxy form. Several of the changes involved in the Bohr effect have been identified. A chloride bridge between the amino terminus of the α chain (valine) and α-141 arginine is broken upon oxygenation of hemoglobin.[551] The imidazole group of the α-chain carboxy terminal histidine forms a salt bridge with the B-94 aspartic acid group which is also broken upon oxygenation.[552] The decrease in pK in each case is approximately 0.8 pH unit.[547] The involvement of chloride in the α-chain salt bridge results in linkage of effects due to hydrogen ion and chloride.[553] A similar effect is seen in the alkaline Bohr effect of hemoglobin.[554] In this case the salt bridge between HIS-146B and ASP-94B is not present in the R form of hemoglobin.[554] This salt bridge forms only when hemoglobin undergoes the R to T state transition. Important salt bridges are given in Table XII.

3. Hemocyanin

Hemocyanin (Hcy) is a copper-containing protein which occurs only in mollusks and arthropods.[11-13] The remarkable size of this non-heme protein is reflected in molecular weights ranging from 400 000 in the prawn *Pandalus borealis* to 8 900 000 in the snail *Helix pomatia*.[13] Single fundamental units of M_r 75 000 have been experimentally obtained for arthropod hemocyanins, each containing two copper(I) ions. Molluscan

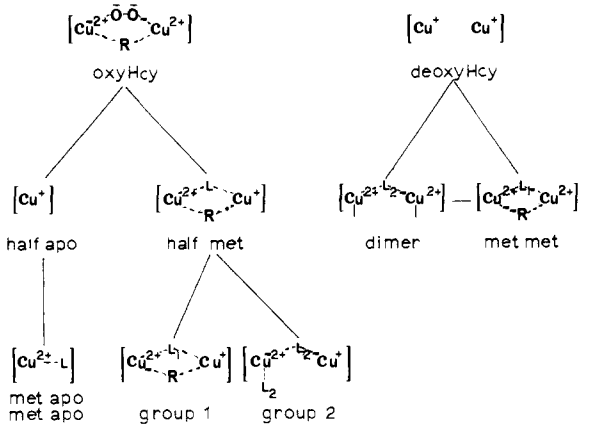


Figure 11. Various active-site derivatives of hemocyanin, where L_1 and L_2 are externally supplied (exogenous) ligands and R is an endogenous ligand.

hemocyanins, on the contrary, dissociate to fundamental units (M_r 380 000–450 000) under normal experimental conditions, which appear to be 20 times the size of the single active site unit. Arthropod and mollusk hemocyanins differ in the amount of copper contained in the protein. Generally, there is approximately 0.17% by weight of copper in the former compared to 0.25% found in the latter.[32] In addition, there is a difference in the catalase activity between the two phyla. High catalase activity is exhibited only by mollusk hemocyanins.[555]

The active site of the protein has been extensively studied by ultraviolet,[30,556] visible,[30,556] resonance Raman,[28,557] EXAFS[558-560] as well as EPR spectroscopy.[30,556] Various active-site derivatives have been prepared and characterized.[30,556] These are summarized in Figure 11. It has been suggested that deoxyhemocyanin contains two-coordinate Cu(I) centers. Two histidine residues comprise the coordination sphere at an average Cu–N distance of 1.95 Å.[560] The Cu(I)–Cu(I) separation is at least 5.6 Å.[560] An earlier EXAFS study suggested the presence of three histidines in the Cu(I) coordination sphere.[558] Some indirect evidence for two-coordination is provided by the reactivity of the Cu(I) complex of α,α'-bis(3,5-dimethylpyrazoyl)-*m*-xylene with CO.[561] Without an auxiliary ligand present, no uptake of CO results. However, in the presence of a coordinating ligand there is binding of one CO/Cu(I) dimer. Since three-coordinate Cu(I) is known to bind CO, it is suggested that only one Cu(I) center is able to add CO.[561] This does not rule out the steric effect of the particular coordinating ligand. However, since the reaction stoichiometry in this simple inorganic system parallels that for Hcy and CO,[562] it seems reasonable to assume two-coordination at the unoxygenated protein active site.

Oxygenation of Hcy gives oxyhemocyanin ($HcyO_2$). The dioxygen is bound between the two Cu(I) centers, giving formally (μ-peroxo)dicopper(II). Such a bonding mode is reminiscent of the (μ-peroxo)dicobalt(III) complexes described previously. Several significant structural changes are evident in the formation of the copper(II) dioxygen complex. As determined by EXAFS,[559] the Cu–Cu separation lessens to 3.55 Å, though still too great for direct metal–metal bonding. The copper increases its coordination number to four, giving approximately square-planar geometry with the Cu–N distance lengthening to 2.01 Å, while the average Cu–O bond is 1.92 Å.[559] Filling the other bridging coordination site is either an endogenous alkoxide ligand[563] or an exogenous OH^- ion.[564] The latter possibility appears reasonable on the basis of the known stability of the corresponding Cu(II) complex. In fact, this type of bonding is found in the hemerythrin protein, which will be discussed in the next section. Coordination by a bridging tyrosine is not at all unreasonable. Contrary to statements by some authors,[559] the high basicity of the phenolic oxygen does not rule out Cu(II)–TYR bonding. The EPR silent oxygenated active site has been interpreted as the result of antiferromagnetic coupling between two Cu(II) d^9 centers through the bridging ligand.[565] Resonance Raman spectroscopy has been used in conjunction with $^{18}O_2/^{16}O_2$ isotope substitution to demonstrate that the dioxygen is indeed bound symmetrically as a μ-peroxo bridge.[566]

The difference in catalase activity discussed earlier has been interpreted in terms of the distortion of the active site.[556] Apparently, the differences in access to axial coordination necessary for an associative peroxide displacement parallels the catalase-like behavior.

Cooperativity and Allosteric Effects. A formal treatment of dioxygen binding to heme proteins has been discussed at some length. Hemocyanins show varying degrees of cooperativity under different experimental conditions. For example, *Callianassa californiensis*[469] (at 25 °C, pH 7.00, TRIS buffer, 0.05 M Mg^{2+}, 0.01 M Ca^{2+}) has $P_{1/2}^{-1} = 5.76$ atm^{-1} and $n = 1.14$, while *Lymnaea stagnalis*[567] (at 20 °C, pH 7.5, 0.01 M HEPES buffer, 0.01 M $CaCl_2$, 0.05 M NaCl) shows stronger dioxygen binding ($P_{1/2}^{-1} = 171$ atm^{-1}) and greater cooperativity ($n = 8.6$). This large variation in n is remarkable but is also much less than would be expected for a protein with 160–200 binding sites. Most hemocyanins show decreasing dioxygen affinity with decreasing pH (normal Bohr effect). There are several cases in which the reverse Bohr effect is seen. This has been thought to be an adaptation to allow dioxygen binding at high levels of CO_2. High levels of Ca^{2+} also increase dioxygen affinity. A connection between this greater loading of dioxygen and the molting cycle of crustaceans has been drawn. During the premolt period metabolic activity rises as does the amount of calcium withdrawn from the exoskeleton.[504] The calcium is stored in various places including the blood.

4. Hemerythrin

The invertebrate phylas sipunculans, polychaetes, priapulids, and brachiopods use an iron-containing protein for dioxygen transport and storage.[8,9,13,568] This protein, hemerythrin (Her), is similar to hemocyanin in several aspects. It contains two metal centers per active site which are coordinated by amino acid residues, rather than by a porphyrin as in hemoglobin and myoglobin. Most of the erythrocyte hemerythrins isolated occur as octamers of M_r 108 000 with two Fe(II) centers in each of the eight identical subunits.[568] Two exceptions to this are *Themiste* (syn. *Dendrostomum*) *pyroides* myohemerythrin (from muscle) with one subunit of M_r 13 900 and *Phascolosoma agassizii* which is a trimer of M_r 40 600.[9] Unlike hemocyanin, hemerythrin has been characterized by single-crystal X-ray diffraction methods.[8,569,570] The quaternary structure

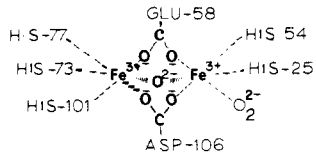


Figure 12. Representation of the active site in oxyhemerythrin. Adapted from ref 569.

of the subunits resembles that of a square antiprism with a 20 × 20 Å channel through the middle.[571,572]

Deoxyhemerythrin has eluded an accurate description of its active site. EXAFS studies have shown marked departure of the coordination environment from other hemerythrin derivatives.[573,574] There is no observable Fe–Fe or Fe–O signal above background, but coordination by histidine is found. Crystal morphology is preserved upon oxygenation of deoxyhemerythrin, thus ruling out any gross (~2 Å) movement of the two "sandwiched" Fe(II) centers.[574] Mössbauer spectra indicate identical Fe(II) environments.[575,576]

Oxyhemerythrin, on the contrary, has been well-characterized. Recent EXAFS studies[573,574] in conjunction with high-resolution X-ray results[8,569,570] have produced a clear picture of the active site as shown in Figure 12. The Fe–Fe separation is 3.57 Å. Each six-coordinate Fe(III) is noticeably nonequivalent, which supports the earlier Mössbauer work.[575,576] There are two bridging carboxylate ligands originating from ASP-106 and GLU-58. Both the μ-oxo bridge and the unsymmetrically bound dioxygen (formally peroxide with $\nu(O_2)$ = 844 cm^{-1}) have been confirmed by $^{18}O_2/^{16}O_2$ isotope experiments with resonance Raman spectroscopy.[577] This type of bonding is unique but resembles the $[Co_2(CN)_4(PMe_2Ph)_5(O_2)]$ system[156] in which two Co(II) centers act as a single two-electron donor. As with hemocyanin, the two Fe(III) centers couple antiferromagnetically via the bridging ligands.[578]

Surprisingly there are very few reports of thermodynamic parameters for dioxygen binding to hemerythrin. For the few data available, $P_{1/2}^{-1} \sim 280$–350 atm^{-1},[458,481,511] which is similar in magnitude to human hemoglobin.

IV. Influence of Bond Type on Free Energies of Dioxygen Complex Formation

The free energy of oxygenation of metal complexes ($\Delta G°_{O_2}$) to form formally $M^{III}O_2(-I,0)$ adducts can be viewed as a combination of various free energy contributions as indicated in eq 68 and 69. Such a par-

$$\Delta G°_{O_2} = \Delta G°_{\sigma\text{-bonding}} + \Delta G°_{\pi\text{-bonding}} + \Delta G°_{\text{electronic}} + \Delta G°_{\text{steric}} + \dots \Delta G°_{\text{solvation}} \quad (68)$$

$$\Delta G°_{O_2} = \sum \Delta G°_i \quad (69)$$

tition of free energy contributions is completely resonable. Logically, oxygenation should depend on properties of the ligand as well as perturbations introduced by the ligand upon complexation to a metal ion. The free energy of oxygenation is related to the oxygenation equilibrium constant by eq 51. In this way the equilibrium constant for oxygenation can be related to the various factors involved in determining the stability of dioxygen complexes. A simple example will serve to illustrate this point. The (μ-peroxo)decaamminedicobalt(III) complex would be expected to have free energy contributions as shown in eq 70. There is no

$$\Delta G°_{O_2} = \Delta G°_{\sigma\text{-bonding}} + \Delta G°_{\pi\text{-bonding}} + \Delta G°_{\text{steric}} + \Delta G°_{\text{electrostatic}} + \Delta G°_{\text{solvation}} \quad (70)$$

free energy contribution due to π bonding since ammonia is a pure σ-donor ligand. Electronic effects would arise from the ligand field contribution to the energy of the d_{z^2} orbital. Since this complex is a binuclear system, one would expect some sort of electrostatic interaction between the charged metal centers. If cyanide replaces the ammonia to form the corresponding (μ-peroxo)decacyanodicobaltate(III) complex, the free energy expression would now include a π-bonding term along with perturbed electrostatic and steric contributions. The major difficulty with this free energy parititon representation lies with the insufficient knowledge of the magnitude of each contribution. Despite this, several free energy relationships for cobalt dioxygen complexes have appeared in the literature.

A word of caution is in order before considering each of the free energy relationships. In general one would naively expect to find linear free-energy relationships in systems which do not vary very differently in structure. That is to say within a given system, with all other factors held constant, a specific observable may vary linearly with an independent parameter. This does not require that every system be described by some formal correlation nor does it maintain that a lack of correlation be indicative of unrelated effects. For each system examined in the following sections, serious consideration of the above points will be made.

σ- and π-Bond Effects. The major contribution to the free energy of oxygenation results from σ bonding. This can be best seen in the qualitative MO diagram given in Figure 13 where Co(II) is coordinated by five equal donor groups. Here the symmetry has been reduced from O_h to C_{4v}; hence the two sets of degenerate metal orbitals also reduce; $t_{2g}(d_{xy},d_{xz},d_{yz}) \rightarrow b_2(d_{xy}) + e(d_{xz},d_{yz})$ and $e_g(d_{z^2},d_{x^2-y^2}) \rightarrow a_1(d_{z^2}) + b_1(d_{x^2-y^2})$. The appropriate ligand orbitals transform as $2a_1 + b_1 + e$ (σ only) and $a_1 + a_2 + b_1 + b_2 + 3e$ (π only). Important metal–ligand bonds are indicated in Figure 13. As the ability of the ligand to donate electron density (ligand donor strength) to the metal center increases, the $a_1(d_{z^2})$ orbital rises in energy. Such an interaction would facilitate the transfer of an electron from a predominantly metal-based MO to a MO with substantial dioxygen character formed from the interaction of a π-acceptor dioxygen ligand (left side of Figure 14). This increase in electron density on the dioxygen ligand (hence more Co(III) character) should result in greater stability of the dioxygen complex.[579]

For a binuclear μ-superoxo complex a qualitative MO diagram can be developed on the basis of the interaction of a $[Co^{III}L_5]^{2-}$ fragment (where the ML_5^{2-} moiety has been constructed with π-acceptor ligands, e.g., CN^-) with O_2^-, followed by interaction with a second $Co^{III}L_5^{2-}$ moiety.[79] Such a combination appears in Figure 14. The internal redox process results in the previously discussed Co^{III}–$O_2(-I,0)$ or Co^{III}–$O_2(-I,-I)$–Co^{III} formalism.

In situations where ligands capable of π bonding are involved two cases must be considered: π donors and π acceptors. Naively, the presence of a π-donor ligand

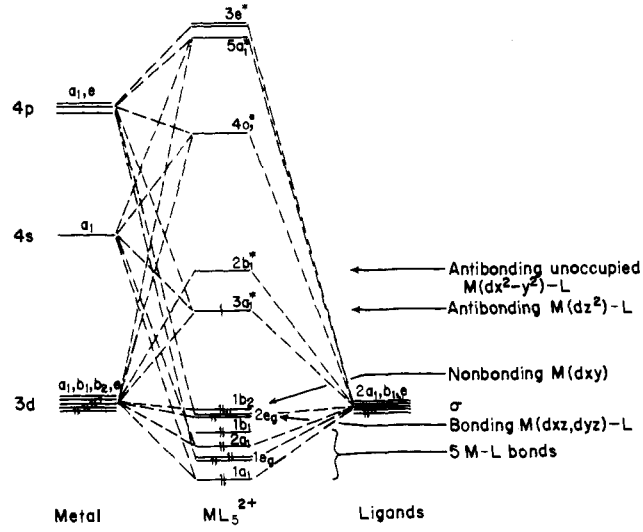


Figure 13. Qualitative molecular orbital diagram for a pentacoordinate metal. Local symmetry is C_{4v}.

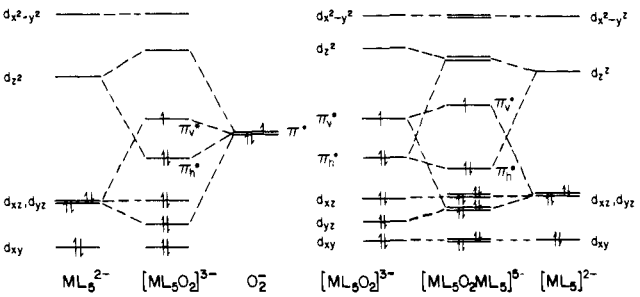


Figure 14. Qualitative molecular orbital diagram for mononuclear superoxopentacyanocobalt(III) and (μ-superoxo)decacyanodicobalt(III) complexes. Adapted from ref 372c.

would introduce orbitals of appropriate symmetry to interact with the doubly degenerate e(d_{xz},d_{yz}) orbitals. Thus π-back-bonding interaction between the cobalt center and dioxygen ligand would be enhanced by this donated electron density. π-Donor ligands will push electron density into the π^*_v MO. Since this is an antibonding MO, localization of the electron density here will destablize the dioxygen complex. It should be noted that the π donor raises the energy of the e(d_{xz},d_{yz}) orbital set. In the latter situation electron density would be less localized on the metal center. Orbital interactions between low-lying empty π^* levels with the degenerate metal e(d_{xz},d_{yz}) set lowers the energy of the resulting bonding MO. As discussed previously the electron transfer which occurs on dioxygen complex formation involves the metal d_{z^2} orbital and the dioxygen π^*_vMO. Occupation of the resulting M–O_2 antibonding MO is generally unfavorable. This interaction may be rendered less unfavorable by withdrawing electron density from the MO. A π-acceptor ligand would do just that.

Although molecular orbital diagrams may help to illustrate the basic principles involved in the formation of stable dioxygen complexes, there can be little understanding of the thermodynamics involved in these systems without the aid of accurate calculations. Even with the benefit of detailed calculations, there are still unanswered questions about these molecular systems. The MO diagram (Figure 14) for a binuclear μ-superoxo complex has been constructed from $[Co^{III}L_5]^{2-}$ and O_2^- fragments. However, the thermodynamics of oxygenation of the system would involve the initial preformed $[Co^{II}L_5]^{3-}$ complex and dioxygen. In order to understand the magnitude of the important contributions to metal dioxygen complex formation, it is necessary to know the electron distribution in the resulting dioxygen complex. This type of treatment would allow the assessment of both the extent of electron transfer (and the amount of charge transfer involved) from the metal center and the amount of electron density appearing on the dioxygen ligand. In the former case electron tranfer to dioxygen and to the other ligands is included.

TABLE XIII. Thermodynamic Data for Monobridged Cobalt Dioxygen Complexes in Aqueous Solution at 25 °C

no.	ligand	log K_{O_2}	ΣpK_a	ref
1.	TETREN	15.83	35.8	581
2.	EPYDEN	14.7	30.6	334, 582
3.	4-IMDIEN	12.6	29.1	430, 582
4.	PYDIEN	11.4	21.6	334, 582
5.	TERPY (PHEN)	6.3	13	148
6.	TERPY (BPY)	5.4	12	148
7.	4-IMDPT	9.5	34.4	430, 582
8.	2-IMDPT	8.6	30.7	430, 582
9.	PYDPT	7.7	27.1	334, 582
10.	HIS	6.6	30.4	151
11.	DAB	7.77	39.2	335
12.	DAP	8.90	33.55	356
13.	TACTD (H_2O)	8.1	26.2	367
14.	TACTD (PYR)	9.2	31.4	367
15.	TACTD (IM)	10.6	33.2	367
16.	TACTD (NH_2)	12.5	35.5	367
17.	TACTD (CN)	>13	35.21	367
18.	HMTACTD (H_2O)	5.6	22.7	367
19.	DGENTA	14.5	18.1	581
20.	$(BPY)_2$	4.2	11.86	354
21.	DAPE	7.17	40.39	356
22.	LYS	5.18	41.8	336
23.	TATTD	8.40	31.03	337
24.	SPYDAE	5.02	17.74	337
25.	TAOTD	2.20	31.92	337
26.	PXBDE (EN)	9.58	37.22	357
27.	PXBDE (GLY)	6.95	32.18	357
28.	PYEN	5.99	16.45	338

A measure of ligand σ basicity is available from protonation constants,[580] and a correlation between the logarithms of the oxygenation constants and the sum of the ligand pKa's exists.[581,582] Monobridged (μ-O_2) complexes (Table XIII, Figure 15) give quite large deviations from the early correlation line.[582] In fact, the range in stability is quite remarkable for complexes with approximately equal ligand basicities (TAOTD, K_{O_2} 2.20, $\sum pK_a$ = 31.92; TACTD(Im), K_{O_2} = 10.6, $\sum pK_a$ = 33.2). Obviously, these deviations suggest differences in structure and bonding of the various cobalt dioxygen complexes. Without introducing additional factors to account for these deviations, there still remain some important relationships. Compounds **1–6** and **20** form a distinct correlation as do the members of the TACTD(X) series (compounds **13–18**) and those ligands which form six-membered chelate rings (compounds **7–9**). Caution should then be exercised when applying the correlation to the prediction of log K_{O_2}. Only those complexes with analogous ligand structures should be employed. As an example of this consider the unrelated ligands **20**, **24**, **18**, **10**, and **11**. These form a very nice correlation which, however, contributes little to the understanding of bonding requirements.

A recent calorimetric study by Timmons et al.[583] has interpreted the thermodynamics of oxygenation as a competition between enthalpic and entropic factors.

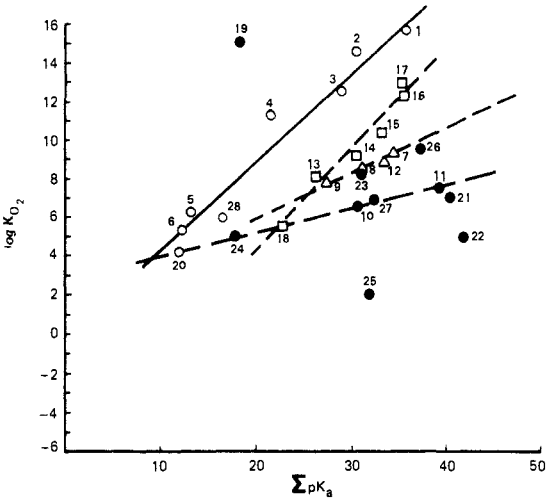


Figure 15. Correlation of log K_{O_2} for monobridged cobalt dioxygen complexes vs. $\sum pK_a$ (○ = related ligands, ● = unrelated ligands, □ = macrocycles, △ = six-membered chelate rings).

PYDPT forms a cobaltous complex with a dioxygen affinity 4 orders of magnitude lower than that of the cobaltous complex of PYDIEN. The smaller enthalpy term for the PYDPT complex is consistent with the observed lengthening of metal–ligand coordinate bonds.[206,207] Cobalt dioxygen complexes of 2- and 4-IMDPT are 3–4 orders of magnitude less stable than the dioxygen complex of 4-IMDIEN. The interesting calorimetric result is that entropic factors oppose the enthalpic factors that are responsible for the reduced stability of the PYDPT, 4-IMDPT, and 2-IMDPT complexes. The entropy differences between PYDIEN and PYDPT complexes and between 4-IMDIEN and 4-IMDPT complexes amount to ~8 kcal/(mol deg). The data in Table XIV indicate a reciprocal relationship between $\Delta H°$ and $\Delta S°$ for these structurally related complexes. The weaker bonding contribution in $\Delta H°$ of oxygenation (which involves both metal–oxygen bond formation and an increment in metal–nitrogen coordinate bonding) is associated with the lesser loss of entropy, which partially compensates for the loss in enthalpy. This is a quite general effect since large increases in coordinate bond energy are expected to restrict molecular freedom, leading to decreases in entropy.

Binuclear cobalt dioxygen complexes with an available additional coordination site cis to the μ-peroxo ligand generally undergo olation. The formation of a μ-hydroxo bridge serves to "lock in" the peroxo oxygen as well as define the steric environment about the complex. Typically, the cobalt–cobalt distance is fixed at approximately 3.25 (2) Å for superoxo complexes and 3.29 (2) Å for peroxo complexes, as compared to the respective monobridged complexes with corresponding Co–Co separation of 4.6 (1) and 4.5 (1) Å, while the corresponding range in dibridged species is only 0.04 Å. Dibridged complexes are forced to assume a cis conformation around the O–O bond, which is the major restriction in the Co–Co separation. Monobridged complexes then possess additional flexibility due to the trans orientation around the O–O bond, which may allow for some dissipation of "strain" energy in these systems. This "strain" energy may involve ligand–ligand interactions (i.e., van der Waals contacts or hydrogen bonding) and metal–metal electrostatic repulsions.

TABLE XIV. Thermodynamic Constants for Oxygenation of Cobaltous Complexes of 4-IMDIEN, 4-IMDPT, PYDIEN, and PYDPT[a]

ligand	$\Delta G°_{298}$, kcal/mol	$\Delta H°_{298}$, kcal/mol	$T\Delta S°_{298}$, kcal/mol	$\Delta S°_{298}$
4-IMDIEN	−17.2 (2)	−33.0 (3)	−15.8 (3)	−53
4-IMDPT	−12.8 (2)	−20.1 (3)	−7.3 (3)	−24
PYDIEN	−15.5 (2)	−32.6 (5)	−17.1 (5)	−57
PYDPT	−10.5 (3)	−19.7 (3)	−9.2 (4)	−31

[a] Adapted from ref 582.

TABLE XV. Thermodynamic Data for (μ-Hydroxo)(μ-peroxo)dicobalt(III) Complexes in Aqueous Solution at 25 °C

no.	ligand	log K_{O_2}	ΣpK_a	ref
1.	$(EN)_2$	10.8	33.94	581
2.	HISTAMINE	8.5	32	409
3.	TRIEN	6.1	28.7	581
4.	TREN	4.4	30.5	362
5.	UDTMA	2.4	24.6	581
6.	SDTMA	2.3	25.3	581
7.	PXTREN	3.69	26.7	338
8.	HEDIEN	1.5	22.5	581
9.	DIEN	1.1	23.2	581
10.	SEDDA	−4.1	16.2	581
11.	UEDDA	−5.3	16.7	581
12.	BPY (2)	−2.6	11.86	354
13.	ALA (2)	−4.03	24.02	151
14.	PRO (2)	4.41	24.6	151
15.	LEU (2)	−4.01	23.10	151
16.	VAL (2)	3.8	23.50	151
17.	DAP (2)	−1.495	32.2	356
18.	BISTREN	−2.58	24.83	359
19.	BISDIEN	−0.42	20.79	360
20.	PYEN	3.83	16.45	348
21.	PYDE	6.26	22.86	338

An appreciable difference between the correlation of log K_{O_2} with $\sum pK_a$ for dibridged dioxygen complexes and the previously discussed monobridged complexes is apparent (Table XV and Figure 16). Except for BISTREN and diaminopropionate (less stable on the basis of ligand basicity) there are only two general correlations found. Certainly π bonding is responsible for the displacement of the pyridine containing ligands from the rest of the series. There is no problem in rationalizing the greater stability of pyridine ligands if π-bonding properties are involved. In view of some recent studies,[206,207,414,583] it has been suggested that this type of ligand may have some π-acceptor character. An explanation based on removing electron density from the metal dioxygen fragment via competition with a different ligand than dioxygen has been outlined previously. It may also be argued that a weak π-acceptor bonding component necessarily enhances the σ component of the M–L bond. Thus ligands with π-bonding capabilities would give not only more stable metal chelates but provide greater metal-centered electron density. Transfer of one electron from Co(II) to coordinated dioxygen gives $Co^{III}–O_2(-I,0)$. In order to stabilize this formal state, strong σ-donating ligands are required.

For binuclear μ-peroxo complexes (formally $Co^{III}–O_2(-I,-I)–Co^{III}$), the two-electron transfer has generated a potential π donor. A metal chelate which possesses ligands with additional π-acceptor character would interact favorably with this π-donor peroxide.

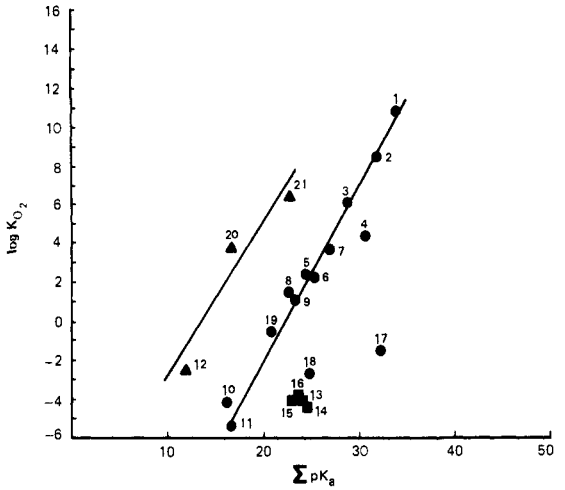


Figure 16. Correlation of log K_{O_2} for dibridged dioxygen complexes vs. $\sum pK_a$ (● = σ-donor ligands, ▲ = pyridine-based ligands, ■ = amino acids).

Since the π^*_g orbital set of the O_2 fragment is fully occupied, only acceptor interactions are important. As mentioned earlier, the presence of low-lying empty ligand π orbitals should lower the energy of some of the important M–L bonding components. Exactly how important this contribution is to the stability of the dioxygen complex formation is unknown. Without the benefit of detailed MO calculations it is impossible to decide upon the more correct interpretation.

The calculated stability of the cobalt dioxygen complexes with pyridine-containing ligands based on the σ-only contributions (assuming the empirical correlation previously established) gives a value which is 3–4 kcal mol^{-1} lower than that measured experimentally. Another plausible explanation may be offered[583] on the basis of the rigid structure of aromatic nitrogen donors. Nitrogen atoms in a rigid planar ring suffer less loss of entropy as well as an increased favorable enthalpy contribution upon complexation than do aliphatic nitrogens. This would be reflected in the $\Delta H°$ and $\Delta S°$ values for complexation by various metal ions. Both steric ring strain ($\Delta H°$) and rotational and vibrational ($\Delta S°$) contributions are more favorable in systems containing aromatic nitrogen bases[583] which parallels the greater stabilities of these complexes over the corresponding aliphatic nitrogen analogues.

It is of interest that the amino acids with similar protonation constants form equally stable dioxygen complexes. In view of the different ligand structures (each of the amino acids has a different R group on the α-carbon), the stabilities of the dioxygen complexes are fairly invariant to these potential steric factors. Some related dipeptide ligands which form dibridged dinuclear dioxygen adducts will be discussed with respect to inductive effects later in this review.

BISTREN[359] serves as an example of the importance of steric effects in determining the stability of the metal dioxygen complex. This cryptand ligand is far less flexible than the analogous macrocyclic binucleating ligand, BISDIEN.[360] Although BISDIEN possesses fewer basic coordinating groups than BISTREN, the formation constant of the cobalt dioxygen complex of BISDIEN is considerably greater than that of BISTREN.

Thermodynamic data are available for the nonaqueous cobalt dioxygen complexes which contain Schiff bases or porphyrin ligands. For such systems, the simple potentiometric method for determining oxygenation constants in aqueous solution must be replaced by a suitable spectrophotometric technique, as discussed previously. σ basicity may again be important in determining the extent of dioxygen complex formation. However, in these nonaqueous systems the precise ligand basicity is not known. Changes in basicity of the axial ligand should provide substantial differences in dioxygen complex formation if bonding to the dioxygen ligand is predominately σ in nature.

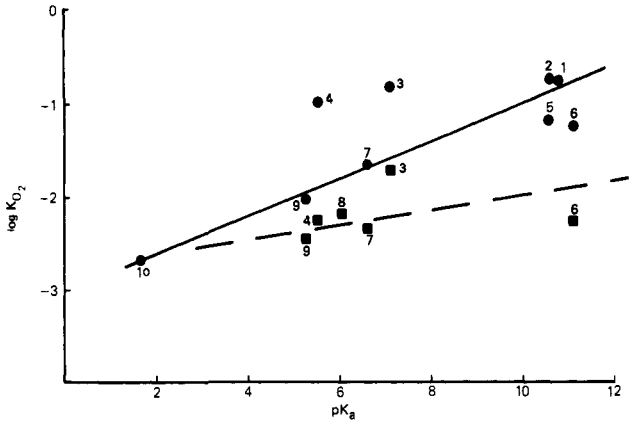


Figure 17. Correlation of log K_{O_2} with pK_a, of the axial ligand, for [Co(BENACEN)B] (●) and [Co(*p*-MeOTPP)B] (■) complexes.

Basolo et al.,[394] Ibers et al.,[421] and Takayanagi et al.[564] have investigated the oxygenation of cobalt(II) Schiff base and cobalt(II) porphyrin type complexes. In general, as the basicity of the axial ligand increases, the formation constants of the dioxygen complexes become greater. Further examination of the thermodynamic data in Tables XVI and XVII suggests additional concepts. Simply confining the correlation to the substituted pyridine ligands in Figures 17 and 18 reflects the previous arguments on ligand basicity. In both systems a dramatic effect can be seen by altering the π-acceptor strength of the axial base. Assuming that, logically, imidazole and *N*-methylimidazole as well as dimethylformamide are stronger π acceptors than pyridine, the fact that they have larger oxygenation constants than the pyridine bases now becomes clear. This is the situation alluded to earlier in this section of the review. Although piperidine is the most basic axial ligand it does not form the most stable dioxygen complex. This has been attributed to unfavorable steric interactions between the piperidine and the porphyrin skeleton.[102,421] It is conceivable that piperidine behaves as a normal aliphatic amine. The lack of π bonding would then explain the lesser stability (compared to imidazole and pyridine).

An additional example of the importance of effects other than σ basicity is found in Table XVIII and illustrated in Figure 19. The series of cobalt(II) mesoporphyrin IX dimethyl ester complexes[584] suggest the general effects of axial ligand basicity. Scatter of these few points probably is a result of at least three factors. Both the size of the donor group and the availability of low-lying (π-acceptor type) d orbitals to participate in bonding may be important in these systems. Also, there is an additional contribution due to the uncertainty in the σ basicity of the ligands. The availability

TABLE XVI. Oxygenation Constants and Polarographic Half-Wave Potentials for Co(BENACEN) and Co(*p*-MeOTPP) Complexes Containing Various Axial Ligands[a]

			Co(BENACEN)		Co(*p*-MeOTPP)	
no.	ligand	pK_a[b]	log K_{O_2},[c] $torr^{-1}$	$E_{1/2}$,[d] mV	log K_{O_2},[c] $torr^{-1}$	$E_{1/2}$,[d] mV
1.	*n*-$BuNH_2$	10.75	−0.75	−740		
2.	*i*-$BuNH_2$	10.57	−0.74	−730		
3.	*N*-MeIm	7.05	−0.82	−720	−1.72	−480
4.	5-Cl-*N*-MeIm	5.45	−0.99	−670	−2.26	−240
5.	*sec*-$BuNH_2$	10.56	−1.18	−620		
6.	PIP	11.1	−1.23	−600	−2.28	−310
7.	3,4-LUT	6.57	−1.66	−560	−2.35	−220
8.	4-MePYR	6.04			−2.20	−230
9.	PYR	5.24	−2.03	−500	−2.46	−200
10.	4-CNPYR	1.64	−2.68	−350		
11.	PPh_3		−3.4	−300		

[a] Adapted from ref 394. [b] Reference 580. [c] 10^{-2} M ligand in toluene at −21 °C; standard state of 1 torr. [d] 10^{-3} M in complex and 0.1 M $Et_4N^+ClO_4^-$, $E_{1/2}$ = ±10 mV vs. SCE taken from anodic wave at hanging drop Hg electrode. [e] Schofield, K. "Hetero-Aromatic Nitrogen Compounds"; Plenum Press: New York, 1967; p 146.

TABLE XVII. Thermodynamic Data for Cobalt(II) Protoporphyrin IX Dimethyl Ester Dioxygen Complexes in Toluene at −45 °C[a]

axial ligand	log K_{O_2}, mm^{-1}	σ^P [b]	pK_a
DMF	−2.27		~2.0
4-CNPYR	−3.8	+0.628	1.64
PYR	−2.84	0.000	5.24[c]
4-*t*-BuPYR	−2.77	−0.197	~6.0
Im	−1.84		7.01[c]
N-MeIm	−1.70		7.05[c]
4-NH_2	−2.05	−0.660	9.16
PIP	−2.35		11.1[c]

[a] Adapted from ref 421. [b] Reference 589, 590. [c] Reference 580.

TABLE XVIII. Thermodynamic Data for Cobalt(II) Mesoporphyrin IX Dimethyl Ester Dioxygen Complexes in Toluene at −80 ± 2 °C[a]

axial ligand	log K_{O_2}, $torr^{-1}$	pK_a
$P(Ph)_3$	−2.4	2.73
$P(Bu)_3$	−0.54[b]	8.43
$P(OMe)_3$	−0.69	3.5
$As(Ph)_3$	−2.8	0.0

[a] Adapted from ref 584. [b] Calculated from ΔH° and ΔS° values for T = −81 °C.

of π bonding in these complexes is thought to be of little importance in comparison to complexes containing unsaturated amines.[584]

Both mononuclear and binuclear dioxygen complexes would be expected to reflect the σ-bonding effects described above in bonding parameters. A careful examination of metal–ligand, metal–oxygen, and oxygen–oxygen bonding parameters (Table VIII) gives some support to this argument. It should be emphasized that some of the differences in specific bond distances and angles are not significant[585] when the standard deviation is considered.

The decaamminedicobalt(II) dioxygen complex has been studied by X-ray diffraction techniques many times. An average O–O distance of 1.47 Å for this compound is characteristic of coordinated peroxide. In the analogous superoxo complex the O–O distance is 1.31 Å, which lengthens slightly to 1.32 Å in the dibridged μ-NH_2-μ-O_2 superoxo species. Upon substituting weaker σ-donor ligands (NH_3, $\sum pK_a$ = 46.60), PYDIEN ($\sum pK_a$ = 21.6), PYDPT ($\sum pK_a$ = 27.1), or

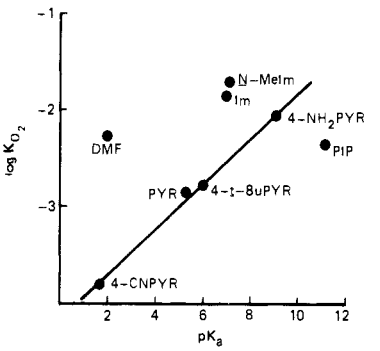


Figure 18. Correlation of log K_{O_2} with pK_a for a series of Co(II) protoporphyrin IX dimethyl ester ligand complexes in toluene at −45 °C.

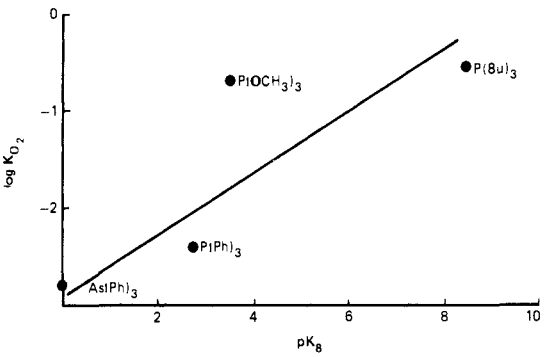


Figure 19. Correlation between log K_{O_2} and pK_a for a series of Co(II) mesoporphyrin IX dimethyl ester ligand complexes in toluene.

EN(DIEN) ($\sum pK_a$ = 40.06), the distance changes to 1.489, 1.456, and 1.488 Å, respectively. Therefore, there appears to be no simple relationship between σ-bonding properties of the ligand and bond distances in the solid state. Steric and electrostatic effects of unknown magnitude may be responsible for the somewhat random fluctuations in O–O bond distances. Specific hydrogen bonding interactions may be present. One must also consider the quality of the crystal structure determination. In many cases the standard deviations of several observations are too large to make valid significant comparisons. Some structure determinations are plagued with disorder (as is the case with several of the mononuclear superoxo complexes where the dioxygen is disordered about a twofold axis).

There are, however, some general trends which are

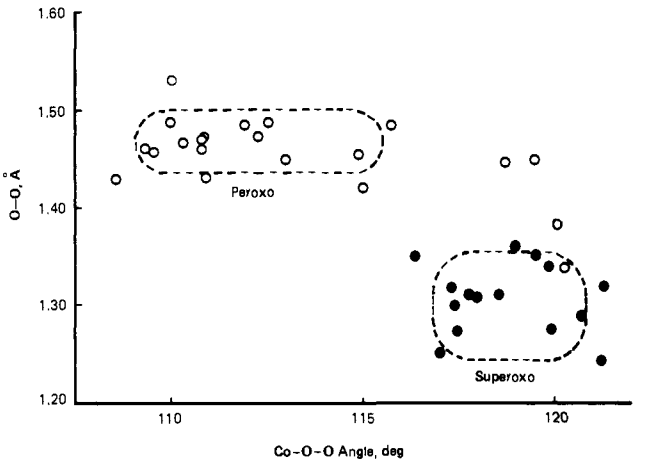


Figure 20. Plot of O–O bond distance vs. Co–O–O bond angle for superoxo (●) and peroxo (○) complexes.

strongly supported by the structural data. Since the dioxygen ligand must accept electron density from the metal center in becoming a superoxo or peroxo moiety, there should be a consequent effect on the trans donor group. Most of the polyamine and Schiff base complexes studies show a lengthening of the M–L1 bond. This bond lengthening is consistent with the facile trans substitution observed in the peroxocobalt(III) complexes.[586] Thus peroxide is an active trans directing ligand. For the simple cobalt dioxygen complexes containing coordinated ammonia, the trans metal–ligand lengthening is observed.

An early study of Audeef and Schaefer[215] reported a correlation between the O–O distance and M–O–O angles. This seemed reasonable because of the limited data base available at the time. Peroxide and superoxide have bond orders of 1 and 1.5, respectively. Bound peroxide should then have a M–O–O angle of 109° (sp^3 hybridization) while superoxide would have a M–O–O angle of 120° (sp^2 hydridization). Extending this relationship to all the known cobalt dioxygen structures gives a scatter plot (Figure 20). Two diffuse regions representing the peroxo and superoxo complexes are indicated on the graph. Generally then peroxo and superoxo ligands have well-separated $r(O_2)$ bond ranges but less resolved Co–O–O angles. Obviously the effects of solvation, ligand interactions, electrostatic forces as well as crystal packing play an important role.

As σ bonding dominates the free energy of oxygenation, π bonding may introduce an important contribution for ligands capable of π bonding. The stability of $[(Co(BIPY)_2)_2O_2(OH)]^{3+}$ (greater than predicted from ligand basicity) is a notable example. Other π contributions have either been discussed previously or will be discussed later in conjunction with more general electronic effects. A comparison of the polyamine-coordinated cobalt dioxygen complexes and the cyano analogues demonstrates some interesting generalizations. Cyanide is a stronger π acceptor than dioxygen and is equally as strong a σ donor as ammonia[580] (based on protonation constants). The r(O–O) for each of the superoxo or peroxo groups do not differ significantly for these ligands. However, the r(Co–O) is longer (weaker bond) for the cyano complexes. The cyano ligand π bonds with the metal, draining electron density from the weaker π-acceptor dioxygen. Thus the Co–O distance should be longer. Also, the trans amine ligand

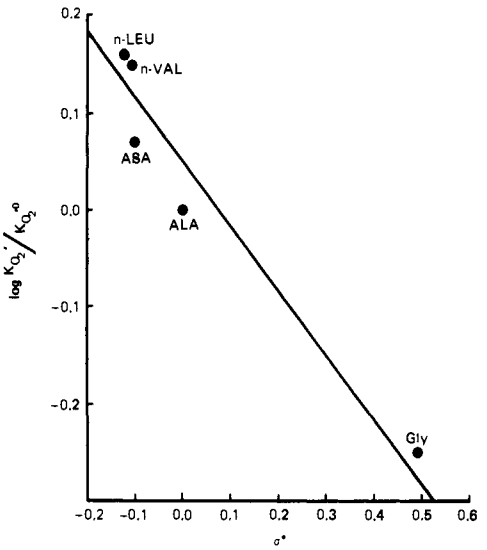


Figure 21. Correlation of log $(K_{O_2}'/K_{O_2}'^{\circ})$ for $[(Co(PHEN)_2L)_2(OH)(O_2)]^{3+}$ vs. σ^*, the net polar alkyl substituent constant, for the amino acid side chains. Adapted from ref 587.

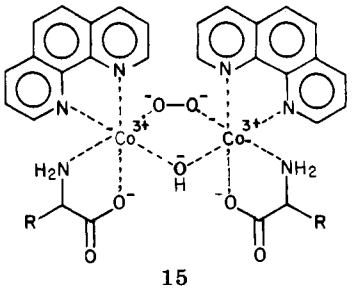
TABLE XIX. Thermodynamic Data for a Series of $(\mu$-OH)$(\mu$-O_2)Bis[phenanthroline-(Amino Acid)]-dicobalt(III) Complexes in Aqueous Solution at 25 °C[a]

amino acid	log $(K_{O_2}'/K_{O_2}'^{\circ})$	σ^* [b]
GLY	−0.25	+0.49
ALA	0.00	0.0
ABA	0.07	−0.1
n-VAL	0.15	−0.115
n-LEU	0.16	−0.130

[a] Adapted from ref 587. [b] References 589, 590.

(in the polyamine complexes) is slightly farther away from the metal as previously discussed, but in the cyano analogue the *trans* ligand is closer to the metal. This is due to the same π-bonding contribution.

Inductive Effects. Several recent equilibrium studies of cobalt dioxygen complexes containing amino acids and dipeptides have suggested a more traditional type of linear free-energy relationship. Palade and co-workers[587] have found a free energy correlation between the oxygenation constant[588] of cobaltous complexes of the type Co(PHEN)L, where L is an amino acid, and the Taft inductive constants, σ^*,[589,590] of the amino acid R group (Figure 21, Table XIX). The slope of the correlation line, ρ^*, has the value −0.621. This satisfies the condition $\rho^* < 0$, which indicates that electron-donating R groups will increase the value of the equilibrium constant.[589,590] Palade rationalizes this as an inductive interaction between the amino acid R group and the nitrogen *trans* to the peroxo ligand. This assumes a similar geometry for the dioxygen complexes as illustrated in **15**.



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Dipeptide ligands provide an additional property

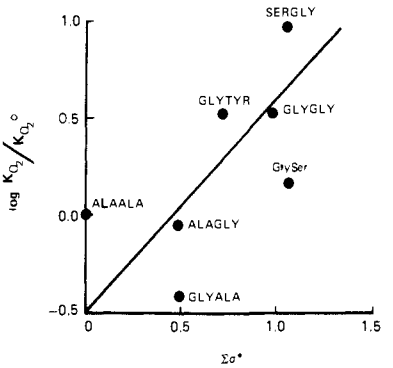


Figure 22. Correlation of log $(K_{O_2}/K^{\circ}_{O_2})$ for cobalt dioxygen complexes containing dipeptide ligands vs. $\sum\sigma^*$, the net polar substituent constants, for the dipeptide side chains.

TABLE XX. Thermodynamic Data for Cobalt(II) Dipeptide Dioxygen Complexes in Aqueous Solution at 25 °C[a]

dipeptide	log $(K_{O_2}/K_{O_2}^{\circ})$	$\Sigma\sigma^*$ [b]
SERGLY	+0.96	1.045
GLYGLY	+0.56	0.980
GLYSER	+0.17	1.045
GLYTYR	+0.56	0.705
ALAGLY	−0.04	0.490
ALAALA	0.0	0.0
GLYALA	−0.41	0.490

[a] Adapted from ref 151. [b] References 589, 590.

which can affect the oxygenation equilibrium. Work by Martell and co-workers has shown amide deprotonation to be an important contribution to the formation of stable dioxygen complexes.[151,316] If the stereochemical environment around the cobalt center is such that the amide nitrogen must be trans to the peroxo group to form a stable dioxygen complex, then any factor which facilitates amide deprotonation should increase K_{O_2}. Loss of the amide proton would be assisted by an electron-withdrawing group located on the α-carbon of the parent amino acid. Although there are actually two inductive contributions in these systems (an additional inductive effect is present on the free amino group), the effect of the deprotonated amide is of greater importance. Figure 22 (and Table XX) shows the relationship between log $(K_{O_2}/K_{O_2}^{\circ})$ and $\sum\sigma^*$ for the dipeptide complexes. In this case the correlation shows some scatter due to the errors involved in determining the magnitudes of the equilibrium constants for metal-promoted amide deprotonation. It does correlate with the general effect described above ($\rho^* > 0$).

Interesting comparisons between inductive effects and resonance contributions are given in Tables XVII, XXI, and XXII. The Co^{II}(PPIXDME) complexes containing substituted pyridines demonstrate inductive effects localized on the axial ligand while the Co^{II}(*p*-X-TPP)(PYR) complexes reflect changes in the equatorial porphyrin ligand. Cummings and co-workers[315] have studied a series of Schiff base complexes containing phenyl-type substituents in the hope of relating inductive effects due to the ligand to dioxygen bonding. Figures 23 and 24 illustrate the relationship between the oxygenation constant and the Taft σ_ρ parameter. The correlation is quite good in both cases with $\rho^* < 0$. Thus, electron-donating groups located at the para position of the benzene ring should increase the degree of formation of the dioxygen complex. However, the

TABLE XXI. Thermodynamic Data for Oxygenation of Cobalt(II) (*p*-X)Tetraphenylporphyrin Pyridine Complexes in Toluene at −72 °C[a]

X	log K_{O_2},[b] M^{-1}	σ^P [c]
OCH_3	3.10	−0.268
CH_3	3.07	−0.170
H	2.98	0.000
F	3.00	0.062
Cl	2.90	0.227
CN	2.76	0.628
NO_2	2.66	0.778

[a] Adapted from ref 366. [b] Standard state is 1 M O_2. [c] References 589, 590.

TABLE XXII. Thermodynamic Data for Oxygenation of Cobalt(III) Schiff Base Pyridine Complexes in Toluene[a,b]

ligand	log K_{O_2},[c] $torr^{-1}$	σ^P [c]
BENACEN	−1.05	0.000
CH_3OBENACEN	−1.01	−0.268
CH_3BENACEN	−1.01	−0.170
BrBENACEN	−0.87	0.232
ClBENACEN	−0.73	0.227
BENSACEN	−1.78	0.000
CH_3OBENSACEN	−1.34	−0.268
CH_3BENSACEN	−0.97	−0.170
BrBENSACEN	−0.76	0.232
ClBENSACEN	−0.62	0.227

[a] Adapted from ref 315. [b] Equilibrium constants are reported for BENACEN-type complexes at −23 °C, BENSACEN-type complexes at −63.5 °C. [c] Standard state is 1 torr. [d] References 589, 590.

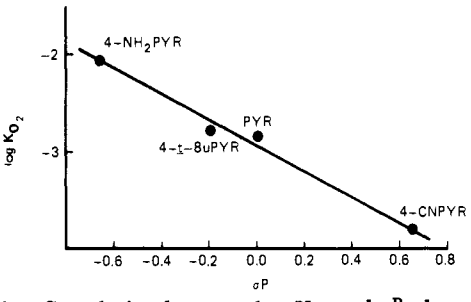


Figure 23. Correlation between log K_{O_2} and σ^P, the para-substituent constant, for a series of Co(II) protoporphyrin IX dimethyl ester complexes with an axial substituted-pyridine ligand in toluene at −45 °C.

apparent correlation in Figure 25 is misleading. In fact, the trend suggests that electron-withdrawing groups at the para position of the aromatic ring would increase the strength of bonding of the dioxygen adduct. However, withdrawing electron density from the metal center would tend to decrease the formation of the dioxygen complex. This situation can be rationalized by considering the nature of the phenyl group in each system. For both of the porphyrin systems the effects are purely inductive, but in the Schiff base system that is not so. The phenyl groups are thought to be coplanar with the rest of the ligand on the basis of the crystal structure of Co(BENACEN)(PYR)O_2.[214] It would be expected then that inductive effects may be secondary to the resonance electron release which is available (indicated in **16** and **17**) which represent part of the Schiff base (chelate). In addition, the stabilities of the sulfur analogues are lower than those of the parent complexes for reasons outlined previously.

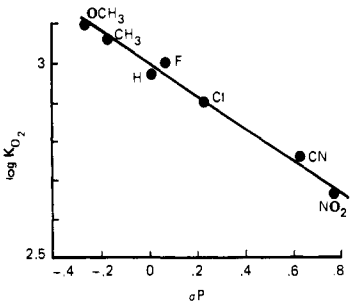


Figure 24. Correlation between log K_{O_2} and σ^P, the para-substituent constant for a series of [Co(*p*-X-TPP)(PYR)] complexes in toluene.

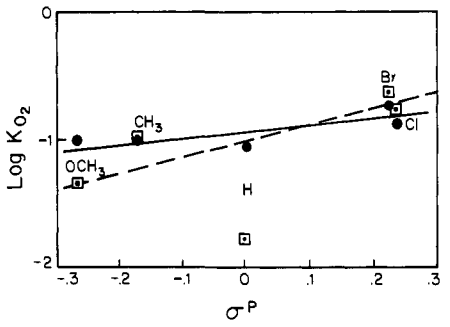
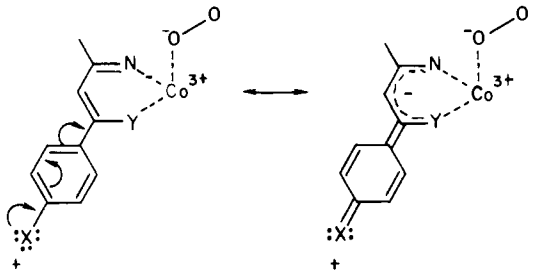


Figure 25. Plot of log K_{O_2} and σ^P, the para-substituent constant, for a (PYR) series of [Co(*p*-X-BENACEN)(PYR)] (●) and [Co(*p*-X-BENSACEN)] (⊡) complexes in toluene.



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Electronic Effects. Another effect which can contribute to a sizable portion of the free energy of oxygenation is ligand field strength. Pickens and Martell[586] have previously shown a linear relationship between the position of the ligand to metal charge-transfer band for cobalt dioxygen complexes and either the reduction potential of the peroxo complex or the oxidation potential for $CoL^{2+} \rightarrow CoL^{3+} + e^-$ (Table XXIII, Figures 26 and 27). Harris et al.[592] have shown that the oxygenation constant for cobalt(II) polyamine complexes is related to the oxidation and reduction potentials of the corresponding cobalt(II) or cobalt(III) complexes as measured at a dropping mercury electrode (Tables XXIV–XXVI and Figures 28–30). Two other groups have noted the linear relationship between log K_{O_2} and the oxidation potential for cobalt(II) complexes[394,593] (Tables XVI and XXVII, Figures 31 and 32). Linear relationships between the oxygen to metal LMCT band energy and the electron affinity of M(II) for $M(O_2)_2$ or the $\bar{\nu}(O_2)$ have been reported by Lever et al.[594] Puxeddu and Costa[355] studied the oxygenation of cobalt(II) Schiff base complexes in pyridine by polarographic methods. There is no apparent correlation between log K_{O_2} and $E_{1/2}$ for the $Co^{2+} \rightarrow Co^{3+}$ oxidation wave (Table XXVIII, Figure 33). This can be attributed to the steric requirement of the substituent of the ethylenediamine which causes different geometries for each of the metal dioxygen complexes. Since $\bar{\nu}$(LMCT) is naively a reverse of the internal electron shift which

TABLE XXIII. Ligand-to-Metal Charge-Transfer Frequencies and the Corresponding Redox Potentials for Some Cobalt Dioxygen Complexes[a]

ligand	$\bar{\nu}$(LMCT), kK	E_{red},[b] mV	E_{ox},[c] mV
TETREN	32.4	−490	−400
EPYDEN	32.0	−410	−410
4-IMDIEN	31.3	−390	−420
PYDIEN	31.3	−340	−310
4-IMDPT	31.0	−210	−240
PYDPT	29.9	−240	−130

[a] Adapted from ref 586. [b] $Co^{3+}LO_2^{2-}Co^{3+}L + e^- \rightarrow Co^{2+}LO_2^{2-}Co^{3+}L$. [c] $Co^{2+}L \rightarrow Co^{3+}L + e^-$.

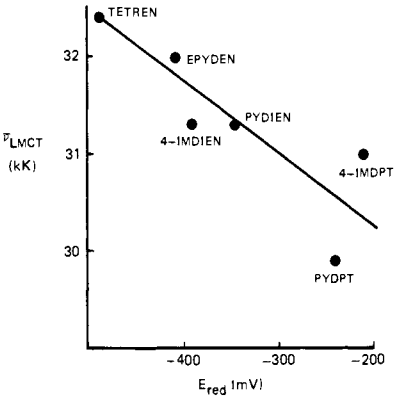


Figure 26. Correlation of $\bar{\nu}$ for $LMCT_b$ transition (the high-energy $Co^{3+} \leftarrow O_2^{2-}$ transition) and the potential for the half-reaction $Co^{3+}LO_2^{2-}Co^{3+} + e^- \rightarrow Co^{2+}LO_2^{2-}Co^{3+}L$.

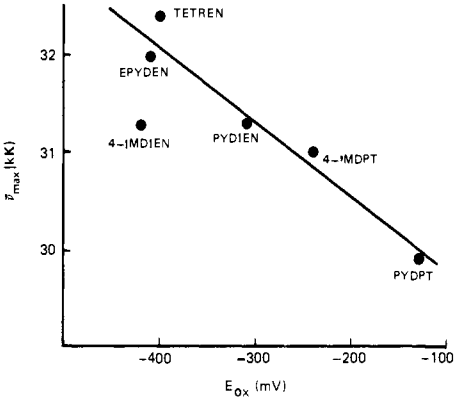


Figure 27. Correlation of $\bar{\nu}$ for the $LMCT_b$ transition (the high-energy $Co^{3+} \leftarrow O_2^{2-}$ transition) and the oxidation potential for $Co^{2+}L \rightarrow Co^{3+}L + e^-$.

TABLE XXIV. Peak Potentials for the Oxidation of Cobaltous Chelates and Their Oxygenation Constants[a]

ligand	$E_{1/2}$, mV	log K_{O_2}[b]
TETREN	−400	15.83
4-IMDIEN	−420	12.57
EPYDEN	−410	14.86
PYDIEN	−310	11.36
PYDPT	−130	7.7
4-IMDPT	−240	9.44
2-IMDPT	−150	8.28
$(HIS)_2$	−30[c]	6.5
$(DAP)_2$	−150[c]	8.9

[a] Adapted from ref 592. [b] Defined in eq 9. [c] Reference 392.

TABLE XXV. Peak Potentials for the Reduction of Co(III) Chelates and the Oxygenation Constants of the Corresponding Co(II) Chelates[a]

ligand	$E_{1/2}$, mV	log K_{O_2}[b]
TRIEN	−420	7.0
EDDA	−200	−4.0
DTMA	−350	2.6
DIEN	−310	1.1
EN	−470	10.8
GLYHIS	−340	1.0[c]

[a] Adapted from ref 592. [b] Defined in eq 9 or 13. [c] $K_{O_2}^{OH} = [Co_2(H_{-1}L)_2O_2(OH)][H^+]/[CoH_{-1}L]^2[O_2]$.

TABLE XXVI. Peak Potentials for a Series of (μ-Peroxo)- and (μ-Peroxo)(μ-hydroxo) dicobalt(III) Complexes[a]

no.	ligand	$E_{1/2}$, mV	log K_{O_2}[b]
	μ-Peroxo Complexes		
1	TETREN	−490	15.83
2	4-IMDIEN	−390	12.57
3	EPYDEN	−410	14.66
4	PYDIEN	−340	11.36
5	PYDPT	−240	7.7
6	4-IMDPT	−210	9.44
7	2-IMDPT	−180	8.28
8	$(HIS)_2$	−100[c]	6.5
9	TERPY(PHEN)	−190	6.3
10	DGENTA	−350	14.5
	μ-Peroxo-μ-Hydroxo Complexes		
11	TRIEN	−530	7.0
12	DTMA	−370	2.6
13	EDDA	−260	−4.0
14	DIEN	−430	1.1
15	GLYHIS	−430	1.0[d]

[a] Adapted from ref 592. [b] Defined by eq 9 or 13. [c] Reference 392. [d] $K_{O_2}^{OH} = [Co_2(H_{-1}L)_2O_2(OH)][H^+]/[Co(H_{-1}L)]^2[O_2]$.

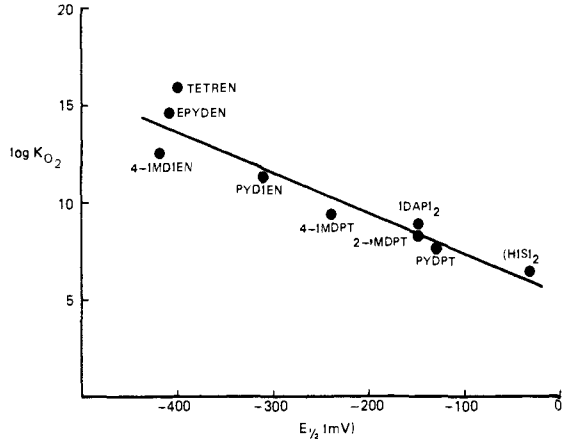


Figure 28. Correlation of log K_{O_2} with the $Co^{2+} \rightarrow Co^{3+}$ peak potentials for cobaltous chelates that form μ-peroxo monobridged complexes.

occurs upon oxygenation and log K_{O_2} depends on the relative energy of the d_{z^2} orbital, a correlation between these would be reasonable. Figure 34 (Table XXIX) shows the correlation for both monobridged and dibridged cobalt dioxygen complexes. It is of interest to compare this correlation with the previous log K_{O_2} vs. $\sum pK_a$ relationship. In the latter case several ligands do not fall into the anticipated stability range (SPYDAE, PYDPT, and DAP). Considering the ligand field strength only, these complexes show closer agreement

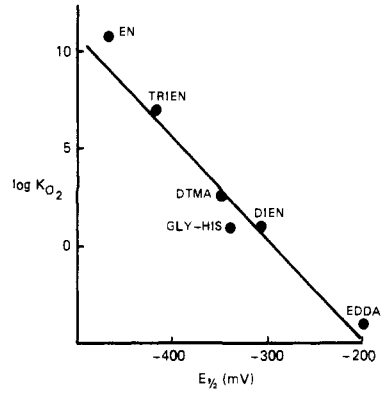


Figure 29. Correlation between log K_{O_2} and $Co^{3+} + e \rightarrow Co^{2+}$ reduction potentials for a series of cobalt chelates that form μ-hydroxo-μ-peroxo dibridged complexes.

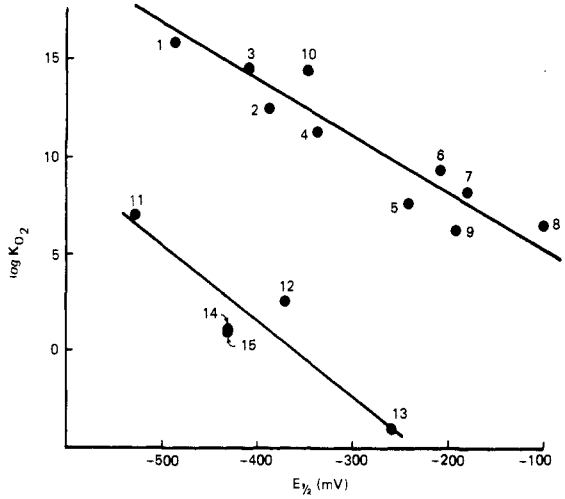


Figure 30. Correlation of log K_{O_2} and the $Co^{3+} + e \rightarrow Co^{2+}$ peak potential for a series of μ-peroxo and μ-hydroxo-μ-peroxo bridged cobalt complexes.

TABLE XXVII. Oxygenation Constants and Polarographic Half-Wave Potentials for Co(L)PYR Complexes[a]

ligand	log K_{O_2},[b] $torr^{-1}$	$E_{1/2}$,[c] mV
ACACEN	−0.28	−590
PhACACEN	−0.89	−550
MeACACEN	−1.12	−540
BENACEN	1.36	−500
SACSACEN	−2.12	−330
p-MeOTPP	−3.1	−230

[a] Adapted from ref 394. [b] Standard state of 1 torr, T = −31 °C. [c] 10^{-3} M complex in 0.1 M Et_4NClO_4 in pyridine, $E_{1/2}$ = ±10 mV vs. SCE taken from anodic wave at hanging drop Hg electrode.

to the predicted empirical stability. Thus the correlation involving log K_{O_2} and the (naively) reverse electron shift between coordinated O_2^{2-} and Co(III) provides a more direct understanding of the electronic requirements for oxygenation.

Resonance Raman spectroscopy has been very useful in identifying LMCT bands. Nakamoto and co-workers have demonstrated the resonance enhancement of $\nu(O_2)$ and $\bar{\nu}$(Co–O) bands.[368,595,597] Using cobalt Schiff base complexes with a variety of axial ligands allows the evaluation of direct effects upon the peroxo or superoxo ligand.[368,598] An increase in the basicity of the axial ligand should result in greater electron transfer to the

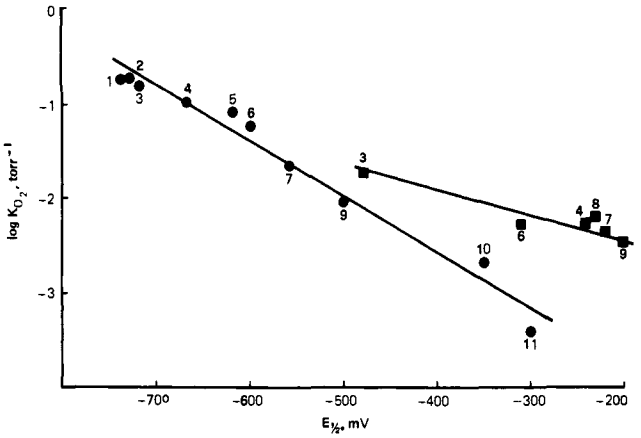


Figure 31. Correlation of log K_{O_2} and the polarographic half-wave potential for a series of [Co(BENACEN)B] (●) and [Co(*p*-MeOTPP)B] (■) complexes.

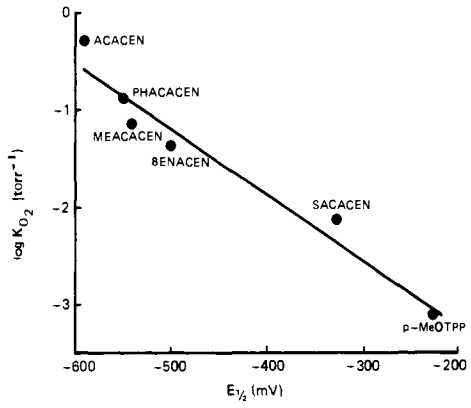


Figure 32. Correlation between log K_{O_2} and the peak oxidation potential for a series of cobalt(II) Schiff base complexes containing an axial pyridine ligand.

TABLE XXVIII. Thermodynamic Data for the Oxygenation of Cobalt(II) Schiff Base Chelates Containing an Axial Pyridine Ligand in Pyridine at 0 °C[a]

no.	ligand	log K_{O_2},[b] M^{-1}	$E_{1/2}$,[c] mV	$E_{1/2}$,[d] mV
1	SALEN	4.2	−395	−705
2	SAL(±)PN	3.6	−357	−650
3	SAL(±)PEN		−361	−642
4	SAL(±)BN	3.4	−364	−700
5	SAL(m)BN	3.5	−285	−710
6	SAL(±)DPEN	1.4	−351	−664
7	SAL(m)DPEN	3.0	−163	−595
8	SAL(±)CHXN	2.4	−360	−651
9	SAL(m)CHXN	2.0	−253	−604

[a] Adapted from ref 355. [b] 0.1 M Et_4NClO_4 in pyridine. [c] $Co^{2+} \rightarrow Co^{3+} + e^-$. [d] $[Co^{2+}LO_2] + e^- \rightarrow [Co^{2+}LO_2]^-$.

dioxygen ligand. As the donation from the metal center increases, the Co–O bond should strengthen and the O–O bond should weaken. This relationship is summarized in Figures 35 and 36 (Tables XXX and XXXI). In both cases there are usually two groups of ligands: those which are pure σ donors and those capable of π interaction. Inspection of the $[(Co(ACACEN)L)_2O_2]$ system[598] allows some speculation about the π contributions in these complexes. The two groups of ligands form parallel linear correlations (Figure 35, bottom), suggesting that the π contribution is a constant increment. However, this is not supported by the [(Co(J-

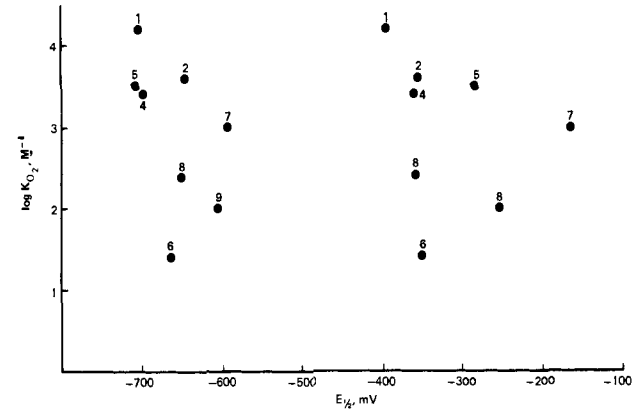


Figure 33. Plot of log K_{O_2} and peak oxidation potential for a series of cobalt(II) Schiff base complexes.

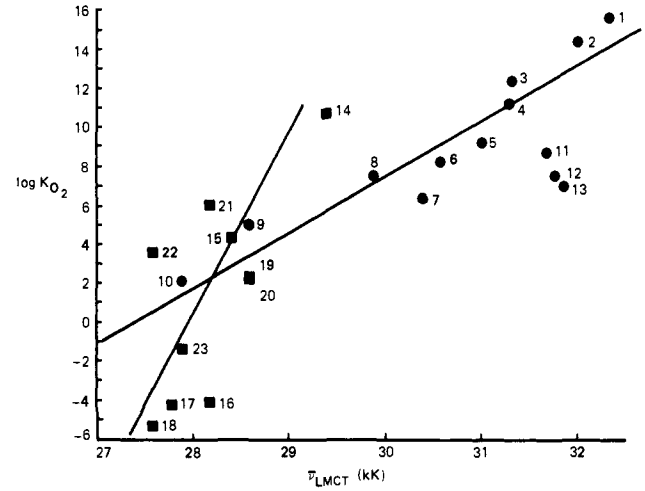


Figure 34. Correlation of log K_{O_2} for monobridged (●) and dibridged (■) cobalt dioxygen complexes with the $LMCT_b$ transition (high-energy $Co^{3+} \leftarrow O_2^{2-}$ transition).

TABLE XXIX. Oxygenation Constants and Ligand-to-Metal Charge-Transfer Frequencies for Some Cobalt Dioxygen Complexes in Aqueous Solution at 25 °C

no.	ligand	log K_{O_2}	ν(LMCT), kK	ref
		μ-Peroxo Complexes		
1	TETREN	15.83	32.4	581, 586
2	EPYDEN	14.7	32.0	334, 582, 586
3	4-IMDIEN	12.6	31.3	430, 582, 586
4	PYDIEN	11.4	31.3	334, 582, 586
5	4-IMDPT	9.4	31.0	430, 582, 586
6	TATTD	8.40	30.6	337
7	HIS	6.5	30.4	151, 411
8	PYDPT	7.7	29.9	334, 582, 586
9	SPYDAE	5.02	28.6	337
10	TAOTD	2.20	27.9	337
11	DAP	8.9	31.7	356
12	DAB	7.77	31.8	335
13	DAPE	7.17	31.9	356
		μ-Peroxo-μ-Hydroxo Complexes		
14	EN	10.8	29.4	349, 581
15	TREN	4.4	28.4	150, 362
16	⟨amino acids⟩	−4.05	~28.2	151
17	SEDDA	−4.24	27.8	350
18	UEDDA	−5.3	27.6	350
19	SDTMA	2.39	28.6	393
20	UDTMA	2.35	28.6	393
21	TRIEN	6.1	28.2	361, 581
22	PXTREN	3.69	27.6	338
23	DAP	−1.495	27.9	356

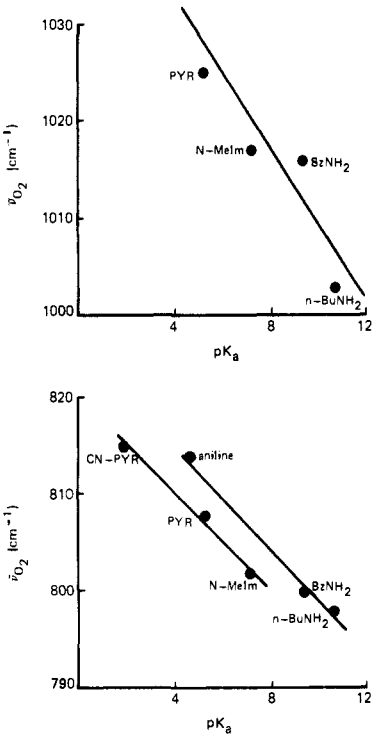


Figure 35. Correlation of $\bar{\nu}_{O_2}$, the O–O stretching frequency, for $[(Co(ACADEN)L)_2O_2]$ with pK_a of the axial ligand (superoxo complexes, top; peroxo complexes, bottom). Adapted from ref 404.

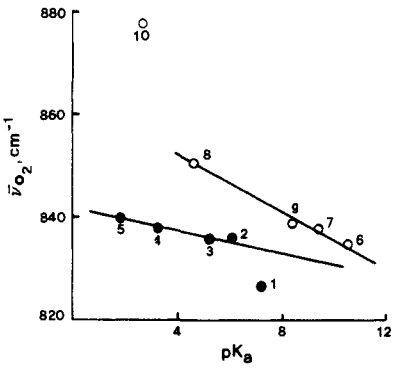


Figure 36. Correlation of $\bar{\nu}_{O_2}$, the O–O stretching frequency, for $[(Co(J\text{-}EN)B)_2O_2]$ with pK_a of the axial base in CH_2Cl_2 at −78 °C; numbers correspond to ligands in Table XXXI. (● = σ-bonding ligands; ○ = ligands involving σ- and π-bonding effects). Adapted from ref 368.

TABLE XXX. Stretching Frequency ($\nu(O_2)$) and Axial Ligand Basicity for $(Co(ACACEN))_2O_2L_2$ Complexes in Dichloromethane[a]

axial ligand	pK_a[b]	$\nu(O_2)$, cm^{-1} 1:1[c]	2:1[c]
4-CNPYR	1.64		815
aniline	4.65		814
PYR	5.24	1025	808
N-MeIm	7.05	1017	802
benzylamine	9.49	1016	800
n-$BuNH_2$	10.75	1003	798

[a] Adapted from ref 598. [b] Reference 580. [c] Metal:dioxygen.

EN)B)$_2O_2$] system.[368] Here the π contribution is not constant since the correlation lines are not parallel.

An additional correlation was expected for cobalt dioxygen complexes containing equal masses of ligands

TABLE XXXI. Oxygen-Oxygen Stretching Frequencies and Basicity of Axial Ligand for $(Co(J\text{-}EN)L)_2O_2$ Complexes in Dichloromethane at −78 °C[a]

no.	axial ligand	pK_a	$\nu(O_2)$, cm^{-1} 2:1[b]	1:1[b]
1	*N*-MeIm	7.05[c]	827	1145
2	4-MePYR	6.04[c]	836	1142
3	PYR	5.24[c]	836	1143
4	Me-*i*-nicotinate	3.26	838	
5	4-CNPYR	1.64[c]	840	
6	*n*-$BuNH_2$	10.75[c]	835	1143
7	benzylamine	9.49[c]	838	1144
8	aniline	4.65[c]	851	
9	$P(Bu)_3$	8.43	839	1136
10	$P(Ph)_3$	2.73	878	

[a] Adapted from ref 368. [b] Metal:dioxygen. [c] Reference 580.

attached to the cobalt. There should be a direct relationship between the logarithms of the oxygenation constants and the frequencies of the O_2 stretching vibrations. However, there are not enough data available to draw any conclusions about this type of relationship.

Solvation Effects. In previous sections the effects of specific solvents have been presented but not formally discussed. Since there appears to be divergent views on the nature of cobalt–dioxygen bonds, it would be beneficial to discuss both and their relationship to solvation effects. Several research groups[93,102,315,368] have suggested that the Co(III)–O_2(–I,0) bond is relatively polar with a dipole resulting from the transfer of an electron from Co(II) to O_2. Much of this polarity, however, is mitigated by the overlap of π-bonding orbitals between the Co(III) and the coordinated superoxide. Oxygenation of cobalt(II) complexes is observed to increase as the solvent changes from the nearly nonpolar solvent toluene to a more polar solvent DMF.[394,404] Binuclear complexes would have two such dipoles which may mutually cancel out, giving an overall symmetrical molecule. Support of this view has been cited in the equilibrium observed in the Co(J-EN)B system.[368] The general observations on this system have been outlined in a previous section. In brief, the equilibrium between binuclear μ-peroxo and mononuclear superoxo complexes was observed to undergo considerable shift in solvents of very low or moderately high polarity. Low polar solvents (based on solvent dipole moments) favor the μ-peroxo dimer. More polar solvents would stabilize the superoxo complex.

A different interpretation of cobalt–dioxygen bonding has been suggested by Martell and co-workers.[579] Binding of dioxygen to cobalt(II) is formally viewed as Co^{III}–O_2(–I,0) with substantial delocalization of electron density on the two oxygen atoms (as well as the cobalt center). Thus the Co–O coordinate bond is polar with a considerable covalent contribution which is amplified by π bonding in the 1:1 superoxo complexes. Although ESR data have suggested significant unpaired electron density on the dioxygen ligand, it does not predict a corresponding amount of charge transfer. Formation of a μ-peroxo binuclear cobalt complex gives more polar Co–O bonds. Evidence for this interpretation is presented in the formation of $Co(s\text{-}Me_2EN)_2(O_2)X$ in EtOH with formation of $(Co(s\text{-}Me_2EN)_2X)_2O_2$ in H_2O (where X is an appropriate anion).

Thermodynamic parameters for the relevant cobalt dioxygen systems in aqueous and nonaqueous solvents

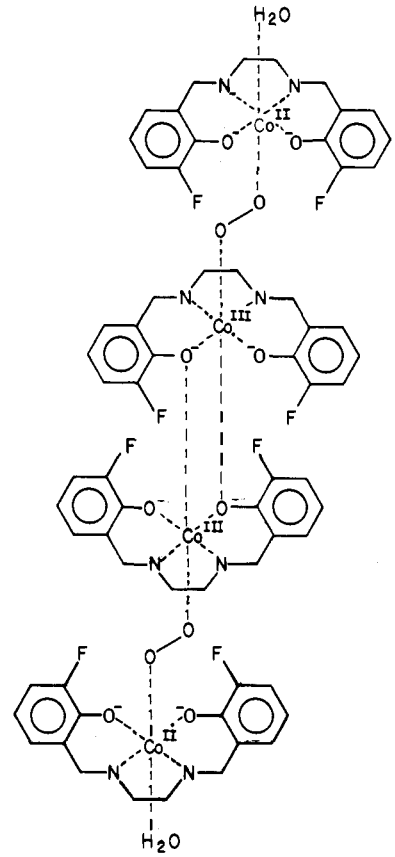
TABLE XXXII. Summary of Thermodynamic Properties for Cobalt(II) Dioxygen Complexes in Aqueous and Nonaqueous Solvents

aqueous solutions	
mononuclear superoxo	$\Delta H^\circ \sim -9.6$ to -11.3 kcal mol^{-1}
	$\Delta S^\circ \sim -58$ eu
polyamines	
binuclear peroxo	$\Delta H^\circ \sim -20$ to -35 kcal mol^{-1}
	$\Delta S^\circ \sim -24$ to -70 eu
nonaqueous solutions	
Schiff base and porphyrins	
mononuclear superoxo	$\Delta H^\circ \sim -5$ to -18.5 kcal mol^{-1}
	$\Delta S^\circ \sim -29$ to -81 eu

factors favoring dioxygen complex formation
1:1 formation: low temperature; high[O_2]; low ϵ solvent
2:1 formation: high temperature; low [O_2]; high ϵ solvent

are summarized in Table XXXII. The enthalpy of formation is more negative for the aqueous systems. This suggests that cobalt–dioxygen bonding is stronger in these systems. In the nonaqueous solvents the entropy term is less favorable (more negative ΔS°). Formation of superoxocobalt Schiff base and cobalt porphyrin complexes in nonaqueous solvents must be concerned with this unfavorable entropy term which necessitates the use of low temperature. At high temperatures the free energy (ΔG°) is dominated by the $T\Delta S^\circ$ contribution, which favors μ-peroxo dimer formation[395] or decomposition.[369,421]

Specific interactions between the solvent and the complexes must be responsible for all of the above observations. Polar solvents should stabilize polar species while nonpolar solvents favor nonpolar species. That is, a reaction which produces products more polar than the reactants should be favored in the former. Reactions which generate products more nonpolar than the reactants would be favored in the latter. Since the dielectric constant is a measure of how well a solvent can stabilize charge separation, it is used here in place of dipole moments. Water then is the best solvent for stabilizing charge separation. It should be noted that water also possesses superior solvating power due to its hydrogen-bonding ability. In addition water has a weak lattice structure which must be disrupted in solvation processes. Lower dielectric constant solvents usually present much less ordered liquid structures than H_2O. The freedom enjoyed in these solvents, on the contrary, magnifies any entropy effects. This is partially due to the somewhat structured nature of water. Consideration should also be given to specific Lewis acid–base interactions involving the solvent and species in solution. An example of this is found in the oxygenation of Co(3-FSALEN) in a mixed $CHCl_3$ piperidine solvent system. The isolated material consists of a dimer of [1,6-bis(2-hydroxy-3-fluorophenyl)-2,5-diaza-1,5-hexadiene]cobalt(III)-μ-superoxo-[1,6-bis(2-hydroxy-3-fluorophenyl)-2,5-diaza-1,5-hexadiene]cobalt(II) hydrate.[220] There are four prominent Co–O interactions (formula 18). One set consists of Co(II)–O_2(0,-I)–Co(III) coordinate bonds while the other two types are Co(II)–H_2O and a Co(III)–O coordinate bond between a Co(III) of one-half of the dimer and a phenolic oxygen derived from a Schiff base ligand on the other half of



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the dimer. Each of these interactions may be characterized by donor–acceptor properties. Apparently the axial H_2O allows the Co(II) to interact somewhat with the coordinated superoxide ligand (r(Co(II)–O_2) = 2.000 Å compared to r(Co(III)–O) = 1.931 Å). The unsymmetrical Co–O bonds may be a result of the different trans axial ligands present.

To this date no mononuclear superoxocobalt(III) complexes in aqueous solution at room temperature have been reported in the literature.[599] This is not surprising since the (μ-peroxo)dicobalt(III) complexes are thermodynamically as well as kinetically more stable.[395] Although the formation of mononuclear adducts may be enhanced in polar nonaqueous solutions, the major destabilizing factor is temperature. On the other hand, a nonpolar and low dielectric constant solvent such as toluene is able to stabilize mononuclear cobalt(II) dioxygen complexes.[314,315,366,394,401-405,421,425] Lowering the temperature greatly decreases the magnitude of the unfavorable $T\Delta S^\circ$ contributions to the overall free energy of oxygenation. At room temperature there are equilibrium amounts of superoxo species, but these are slowly depleted through both the dimerization reaction and decomposition pathways.[369,395,421] Water has the exceptional ability to stabilize highly charged centers regardless of the balancing of dipoles through molecular symmetry (i.e., the solvated water sees the microscopic polar parts of each solute molecule rather than the molecule as a whole). This is probably the reason why (μ-peroxo)dicobalt(III) species rather than the mononuclear superoxocobalt(III) species are far more stable in aqueous solution. The Co(J-EN)B system is interesting since it suggests that some other factors may be more important in determining the stoichiometry of dioxygen binding. Further studies of

this type should be carried out to determine if this kind of behavior is unique or more general.

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V. Glossary

ABA	aminobutyric acid
2-X-ACACEN	1,12-dihyroxy-4,9-dimethyl-3,10-di-X-5,8-diaza-2,4,8,10-dodecatetraene
ACE	acetone
ALA	alanine
ALAALA	alanylalanine
ALAGLY	alanylglycine
ARG	arginine
ASN	asparagine
ASP	aspartic acid
ASPGLY	aspartylglycine
B_{12r}	vitamin B_{12r}
p-X-BENACEN	1,10-dihydroxy-3,8-dimethyl-1,10-bis(3-X-phenyl)-4,7-diaza-1,3,7,9-decatetraene
p-X-BENSACEN	1,10-dimercapta-3,8-dimethyl-1,10-bis(3-X-phenyl)-4,7-diaza-1,3,7,9-decatetraene
BHD	bicyclo[2.2.1]hepta-2,5-diene
BIMP	2,6-bis[1-[(2-imidazol-4-ylethyl)imino]ethyl]-pyridine
BISDIEN	1,4,10,13,16,22-hexaaza-7,19-dioxacyclotetracosane
BISTREN	1,4,10,13,16,22,27,33-octaaza-7,19,30-trioxabicyclo[11.11.11]pentatriacontane
BIS-TRIS	bis(2-hydroxyethyl)aminotris(hydroxymethyl)-methane
BPY	2,2′-bipyridine
Bz	benzene
BzIm	1-benzylimidazole
Chl	chlorocruorin
CNPYR	cyanopyridine
COD	1,5-cyclooctadiene
CoHb	cobalt hemoglobin
COLL	γ-collidine
DAB	L-2,4-diaminobutanoic acid
DAP	DL-2,3-diaminopropanoic acid
DAPE	L-2,5-diaminopentanoic acid
DCC-$(R_1)(R_2)$	R_1 = H, R_2 = $(CH_2)_4$, 3,7,11,15,18,23-hexaaza-2,8,17,24-tetramethylbicyclo[8.7.7]tetracosa-1,2,7,9,10,15-hexaene; R_1 = CH_3, R_2 = $(CH_2)_6$, 3,7,11,15,18,25-hexaaza-2,8,17,18,25,26-hexamethylbicyclo[10.7.7]hexacosa-1,2,7,9,10,15-hexaene
DCHIm	1,5-dicyclohexylimidazole
DGENTA	diglycylethylenediaminetetraacetic acid
DIEN	diethylenetriamine
DMAP	4-(dimethylamino)pyridine
DME	1,2-dimethoxyethane
DMF	*N*,*N*-dimethylformamide
DMTAD	4,7-dimethyl-1,4,7,10-tetraazadecane
2,3-DPG	2,3-diphosphoglycerate
DPIX-DME	deuteroporphyrin IX dimethyl ester
DTAHD	2,4-dioxo-1,5,8,11,14-pentaazahexadecane
DTDA	diethylenetriamine-1,7-diacetic acid
EDTA	ethylenediaminetetraacetic acid
EN	ethylenediamine
EPR	electron paramagnetic resonance
EPYDEN	2,6-bis[5-(1,4-diazahexyl)]pyridine
Ery	erythrocruorin
EtOH	ethanol
EXAFS	extended X-ray absorption fine structure
FARS	(*R*,*R*:*S*,*S*)-1,2-bis(*As*-methyl-*As*-dimethylarsinopropyl)diarsinobenzene
FeCu-4	iron–copper cofacial diporphyrin with four-atom bridge between porphyrins
FeCu-5	iron–copper cofacial diporphyrin with five-atom bridge between porphyrins
FeSP-15	iron strapped heme porphyrin with 15-carbon chain between amide straps
GLU	glutamic acid
GLY	glycine
GLYALA	glycylalanine
GLYASP	glycylaspartic acid
GLYGLY	glycylglycine
GLYHIS	glycylhistidine
GLYLEU	glycylleucine
GLYSER	glycylserine
GLYTYR	glycyltyrosine
GLYVAL	glycylvaline
Hb	hemoglobin
HbO_2	oxyhemoglobin
Hcy	hemocyanin
$HcyO_2$	oxyhemocyanin
HEDIEN	*N*-(2-hydroxyethyl)diethylenetriamine
HEPES	*N*-(2-hydroxyethyl)piperazine-*N*′-2-ethanesulfonic acid
Her	hemerythrin
$HerO_2$	oxyhemerythrin
HIS	histidine
HISGLY	histidylglycine
HISHIS	histidylhistidine
HMPA	hexamethylphosphoramide
HMTA-CTD	5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraaza-4,11-cyclotetradecadiene
Hv	hemovanadin
IHP	*myo*-inositol hexakis(dihydrogen phosphate)
Im	imidazole
4-IMDIEN	1,9-bis(4-imidazolyl)-2,5,8-triazanonane
2-IMDPT	1,11-bis(2-imidazolyl)-2,6,10-triazaundecane
4-IMDPT	1,11-bis(4-imidazolyl)-2,6,10-triazaundecane
IMEN	1,6-bis(4-imidazolyl)-2,4-diazahexane
J-EN	3,10-diacetyl-2,11-dihydroxy-5,8-diaza-2,4,8,10-dodecatetraene
Lgb	leghemoglobin
$LgbO_2$	oxyleghemoglobin
LUT	lutidine
LYS	lysine
Mb	myoglobin
MbO_2	oxymyoglobin
MeCN	acetonitrile
s-Me_2EN	*N*,*N*′-dimethylethylenediamine
N-MeIm	*N*-methylimidazole
Me_2Im	1,2-dimethylimidazole
MeO-BHCP	5-methoxybicyclo[2.2.1]heptano-β-cyclopentene
MeOH	methanol
MePYR	methylpyridine
Me_2SO	dimethyl sulfoxide
MetHb	methemoglobin
MetMb	metmyoglobin
MPIX-DME	mesoporphyrin IX dimethyl ester
MPIX-IPA	mesoporphyrin IX with covalently attached *N*-[3-(1-imidazolyl)propyl]amide
MP-MPP	mesoporphyrin IX with covalently attached monopyridinepropanol
NHE	normal hydrogen electrode
NMR	nuclear magnetic resonance
OEP	octaethylporphyrin

$P_{1/2}$	pressure of dioxygen necessary for half-oxygenation of the system
PABNDT	3,6,10,13,19-pentaazabicyclo[13.3.1]nonadeca-1-(19),15,17-triene
PACH	1,4,7,10,13-pentaazacyclohexadecane
PACP	1,4,7,10,13-pentaazacyclopentadecane
PAPD	1,5,8,11,15-pentaazapentadecane
PHEN	1,10-phenanthroline
2-PHOS	*cis*-1,2-bis(diphenylphosphino)ethene
PIC	picoline
PImSG	polymer-supported imidazolylpropylsilica gel
PIP	piperidine
Piv_3-(4CIMP)P	α,β,γ-tris(*o*-pivalamidophenyl)-δ-[*o*-(3-*N*-imidazolylbutyramido)phenyl]porphyrin
Piv_3-(5CIMP)P	α,β,γ-tris(*o*-pivalamidophenyl)-δ-[*o*-(3-*N*-imidazolylvaleramido)phenyl]porphyrin
PPIX-DME	protoporphyrin IX dimethyl ester
PXBDE	tetrakis(2-aminoethyl)-α,α'-diamino-*p*-xylene
PXTREN	1,4-bis(2-(3-azapropyl)-2,5,8-triazaoctyl)benzene
PYDE	1-(2-pyridyl)-2,5,8-triazaoctane
PYDIEN	1,9-bis(2-pyridyl)-2,5,8-triazanonane
PYDPT	1,11-bis(2-pyridyl)-2,6,10-triazaundecane
PYEN	1,6-bis(2-pyridyl)-2,5-diazahexane
PYP-IPA	pyrroporphyrin with covalently attached *N*-[3-(1-imidazolyl)propyl]amide
PYR	pyridine
σ_p	Taft inductive constant for parasubstituted groups in benzoic acid series
σ_p	Taft polar constant for hydrocarbon series
SACSACEN	2,11-dimercapta-4,9-dimethyl-5,8-diaza-2,4,8,10-dodecatetraene
SALBN	3,4-dimethyl-1,6-bis(2-hydroxyphenyl)-2,5-diaza-1,5-hexadiene
SALCHXN	1,2-bis(4-hydroxy-1-aza-1,3-pentadienyl)cyclohexane
SALDAPE	1,11-bis(2-hydroxyphenyl)-2,10-diaza-6-oxa-1,10-undecadiene
SALDPEN	3,4-diphenyl-1,6-bis(2-hydroxyphenyl)-2,5-diaza-1,5-hexadiene
X-SALDPT	1,11-bis(2-hydroxy-X-phenyl)-2,6,10-triaza-1,10-undecadiene
SALEN	1,6-bis(2-hydroxyphenyl)-2,5-diaza-1,5-hexadiene
SALMDPT	6-methyl-1,11-bis(2-hydroxyphenyl)-2,6,10-triaza-1,10-undecadiene
SALMEN	3-methyl-1,6-bis(2-hydroxyphenyl)-2,5-diaza-1,5-hexadiene
SALPEEN	3-[2-(2-pyridyl)ethyl]-1,6-bis(2-hydroxyphenyl)-2,5-diaza-1,5-hexadiene
SALPEN	3-phenyl-1,6-bis(2-hydroxyphenyl)-2,5-diaza-1,5-hexadiene
SALPR	1,7-bis(2-hydroxyphenyl)-2,6-diaza-1,6-heptadiene
3-X-SALTMEN	1,6-bis(2-hydroxy-3-X-phenyl)-3,3,4,4-tetramethyl-2,5-diaza-1,5-hexadiene
SCE	saturated calomel electrode
SDTMA	*N*,*N*-bis(2-aminoethyl)glycine
SEDDA	*N*,*N*'-ethylenediaminediacetic acid
SERGLY	serylglycine
SPYDAE	1,9-bis(2-pyridyl)-2,8-diaza-5-thianonane
TACD	1,4,7,10-tetraazacyclododecane
TACH	1,4,10,13-tetraaza-7-oxacyclohexadecane
TACT	1,4,7,10-tetraazacyclotridecane
TACTD	1,4,8,11-tetraazacyclotetradecane
7-TACTD	1,4,7,11-tetraazacyclotetradecane
TAOTD	1,4,10,13-tetraaza-7-oxatridecane
TATTD	1,4,10,13-tetraaza-7-thiatridecane
TERPY	2,2':6',2''-terpyridine
TETREN	tetraethylenepentaamine
THF	tetrahydrofuran
THPIm	5,6,7,8-tetrahydroimidazo[1,5-*a*]pyridine
THTP	tetrahydrothiophene
TPivPP	*meso*-$\alpha,\beta,\gamma,\delta$-tetrakis(*o*-pivalamidophenyl)-porphyrin
TPP	*meso*-tetraphenylporphyrin
p-X-TPP	para-substituted *meso*-tetraphenylporphyrin
TPP-AAB1	α,β,γ-tris(*p*-methylphenyl)-δ-(*o*-R-phenyl)-porphyrin (R = $O(CH_2)_4CONHPYR$)
TPP-AAB2	α,β,γ-tris(*p*-methylphenyl)-δ-(*o*-R-phenyl)-porphyrin (R = $O(CH_2)_3CONHPYR$)
TREN	tris(2-aminoethyl)amine
TRIEN	triethylenetetraamine
TRIS	tris(hydroxymethyl)aminomethane
TYR	tyrosine
UDTMA	*N*-diethylenetriamineacetic acid
UEDDA	*N*,*N*-ethylenediaminediacetic acid
VAL	valine

VI. Appendix I

Appendix I consists of data on the thermodynamics of formation of synthetic dioxygen complexes (Table XXXIII).

VII. Appendix II

Appendix II consists of data of equilibrium constants for reaction of natural oxygen carriers and modified natural oxygen carriers with O_2 (Table XXXIV).

Registry No. O_2, 7782-44-7.

VIII. References

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TABLE XXXIII. Thermodynamics of Formation of Synthetic Dioxygen Complexes

A. Equilibrium Constants for Reactions of Co(II) Complexes with O_2 in Aqueous Solution

complex	T, °C	μ, M	log K_{O_2}[a]	log K_{O_2}'[b]	$P_{1/2}^{-1}$,[c] atm^{-1}	other constants	ref
				I. μ-Peroxo-Bridged Products			
$[Co(NH_3)_5(H_2O)]^{2+}$[d]	25					log K_{O_2} = 6.3 × 10^6 M^{-2},[e] $\Delta H°$ = 30 kcal mol^{-1}	339
$[Co(TETREN)]^{2+}$	25	0.10				log K = 38.7 (0.2) M^{-3} atm^{-1} [f]	347
	25	0.10	15.83 (6)	43.15 (6)	9.1 × 10^9		334, 581, 582
			>10				409
$[Co(PYDIEN)]^{2+}$	25	0.10	11.4 (1)	40.8 (1)	3.4 × 10^5	$\Delta G°_{298}$ = −15.5 (2) kcal mol^{-1}, $\Delta H°_{298}$ = −32.6 (5) kcal mol^{-1}, $\Delta S°_{298}$ = −57 eu	334, 582, 583
			~12				340
$[Co(PYDPT)]^{2+}$	25	0.10	7.7 (2)	30.6 (2)	6.8 × 10^1	$\Delta G°_{298}$ = −10.5 (3) kcal mol^{-1}, $\Delta H°_{298}$ = −19.7 (3) kcal mol^{-1}, $\Delta S°_{298}$ = −31 eu	334, 582, 583
$[Co(EPYDEN)]^{2+}$	25	0.10	14.7 (1)	4.26 (1)	6.8 × 10^8	$\Delta G°_{298}$ = −20.1 (2) kcal mol^{-1}, $\Delta H°_{298}$ = −34.2 (3) kcal mol^{-1}, $\Delta S°_{298}$ = −47 eu	334, 582, 583
$[Co(4\text{-}IMDIEN)]^{2+}$	25	0.10	12.6 (1)[g]	40.3 (1)[g]	5.4 × 10^6	$\Delta G°_{298}$ = −17.2 (1) kcal mol^{-1}, $\Delta H°_{298}$ = −33.0 (3) kcal mol^{-1}, $\Delta S°_{298}$ = −53 eu	430, 582, 583
$[Co(4\text{-}IMDPT)]^{2+}$	25	0.10	9.4 (1)[g]	32.2 (1)[g]	3.4 × 10^3	$\Delta G°_{298}$ = −12.8 (2) kcal mol^{-1}, $\Delta H°_{298}$ = −20.1 (3) kcal mol^{-1}, $\Delta S°_{298}$ = −24 eu	430, 582, 583
	25	0.10	9.49 (3)[h]	32.21 (3)[h]	4.2 × 10^3		430, 582
$[Co(2\text{-}IMDPT)]^{2+}$	25	0.10	8.3 (1)[g]	31.4 (1)[g]	2.7 × 10^2		430, 582
	25	0.10	8.63 (1)[h]	31.73 (1)[h]	5.8 × 10^2		430, 582
$[Co(TERPY)(BPY)]^{2+}$	25	0.10	7.13 (7)[h]		1.8 × 10^1		148, 581
	25	0.10	6.30 (7)[i]		2.7		148, 581
$[Co(TERPY)(PHEN)]^{2+}$	25	0.10	6.85 (7)[h]		9.6		148
	25	0.10	6.23 (7)[i]		2.3		148
	25	0.10	5.4		3.4 × 10^{-1}		581
[Co(DTDA)]	20		6.62 (2)			given as K_{O_2} = 4.1 (0.3) × 10^6 M^{-2}	341
$[Co(L\text{-}DAB)_2]$	25	0.10	7.77 (4)		7.9 × 10^1		335
	30		6.86			$\Delta H°$ = −26.7 kcal mol^{-1}	392
$[Co(DL\text{-}DAP)_2]$	25	0.10	8.90 (8)		1.1 × 10^3		356
	30		7.96			$\Delta H°$ = −29.3 kcal mol^{-1}	392
[Co(L-DAPE)(HDAPE)]$^+$	25	0.02	7.17 (12)				356
$[Co(HIS)_2]$	25	0.10	6.50 (10)		4.3		151
	24	0.20	6.86 (4)			$\Delta H°$ = −36 kcal mol^{-1}	342
	15	0.20	7.49 (4)				342
	30		5.82			$\Delta H°$ = −25.5 kcal mol^{-1}	392
	25	0.02	6.63 (5)			$\Delta G°$ = −9.05 (7) kcal mol^{-1}, $\Delta H°$ = −30.1 (1.3) kcal mol^{-1}, $\Delta S°$ = −70 (5) cal deg^{-1} mol^{-1}	343, 581
[Co(GLYALA)]	25	0.10				log $K_{O_2}^2$ = −11.68 (3),[j] log $K_{O_2}^0$ = 7.43 (3)[k]	151
[Co(GLYSER)]	25	0.10				log $K_{O_2}^2$ = −11.19 (1),[j] log $K_{O_2}^0$ = 8.01 (1)[k]	151
[Co(SERGLY)]	25	0.10				log $K_{O_2}^2$ = −10.70 (2),[j] log $K_{O_2}^0$ = 8.80 (2)[k]	151
[Co(ALAALA)]	25	0.10				log $K_{O_2}^2$ = −12.16 (3),[j] log $K_{O_2}^0$ = 7.84 (3)[k]	151
[Co(GLYTYR)]	25	0.10				log $K_{O_2}^2$ = −12.6 (2),[j] log $K_{O_2}^0$ = 8.4 (2)[k]	151
[Co(GLYGLY)]	25	0.10				log $K_{O_2}^2$ = −12.2 (2),[j] log $K_{O_2}^0$ = 8.4 (2)[k]	151
[Co(ALAGLY)]	25	0.10				log $K_{O_2}^0$ = 7.8 (2)[k]	151
[Co(GLYVAL)]	25	0.10				log $K_{O_2}^2$ = −13.5 (5),[j] log $K_{O_2}^0$ = too low for accurate determination[k]	151
[Co(GLYLEU)]	25	0.10				log $K_{O_2}^2$,[j] log $K_{O_2}^0$ = too low for accurate determination[k]	151
$[Co(TACTD)(H_2O)]^{2+}$	25	0.10	8.1 (1)[l]		1.7 × 10^2		367
$[Co(TACTD)(PYR)]^{2+}$	25	0.10	9.2 (2)[l]		2.1 × 10^3		367
$[Co(TACTD)(Im)]^{2+}$	25	0.10	10.6 (2)[l]		5.4 × 10^4		367
$[Co(TACTD)(NH_3)]^{2+}$	25	0.10	12.5 (5)[l]		4.3 × 10^6		367
$[Co(TACTD)(CN)]^+$	25	0.10	>13[l,m]				367
$[Co(HMTACTC)(H_2O)]^{2+}$	25	0.10	5.6 (3)[l]		5.4 × 10^{-1}		367
$[Co(DGENTA)]^{2+}$	25	0.10				log K_{O_2} = −38.5 (2)[n]	391
	25	0.10	14.5		4.3 × 10^8		581

$[Co(EN)_2]^{2+}$	25	1.0				$\Delta G^\circ = -10$ kcal mol^{-1}, $\Delta H^\circ = -29.4$ kcal mol^{-1}, $\Delta S^\circ = -65$ cal deg^{-1} mol^{-1}	343
$[Co(BPY)_2]^{2+}$	25	0.1	4.2		2.1×10^{-2}		354
$[Co(PHEN)_2]^{2+}$	25	0.10			4.6×10^{-2}	log $K = 4.53^p$	344
$[Co(PHEN)(GLY)]^{2+}$	25	0.10			5.9×10^{-3}	log $K = 3.64$	363
$[Co(PHEN)(ALA)]^{+}$	25	0.10			1.0×10^{-2}	log $K = 3.89$	363
$[Co(PHEN)(ABA)]^{+}$	25	0.10			1.2×10^{-2}	log $K = 3.96$	363
$[Co(PHEN)(n\text{-VAL})]^{+}$	25	0.10			1.5×10^{-2}	log $K = 4.04$	363
$[Co(PHEN)(n\text{-LEU})]^{+}$	25	0.10			1.5×10^{-2}	log $K = 4.05$	363
$[Co(CYCLAM)]^{2+}$	35	0.20	1.7 (1)	27.1		$K_{ML} = 5.1\ (8) \times 10^{12}$	345
$[Co(PACP)]^{2+}$	35	0.20	dec			log $K_{ML} = 16.76$ (5)	346
$[Co(PACH)]^{2+}$	35	0.20	7.87 (5)	39.77 (5)		log $K_{ML} = 15.95$ (5)	346
$[Co(TACH)]^{2+}$	35	0.20	4.64 (5)	27.48 (5)		log $K_{ML} = 11.42$ (5)	346
[Co(LYS)]	25		5.18[g]				336
$[Co(TATTD)]^{2+}$	25	0.10	8.40 (1)	31.32 (1)	3.4×10^{2}	log $K_{ML} = 11.46$ (1), log $K_{MHL} = 4.29$ (5)	337
$[Co(SPYDAE)]^{2+}$	25	0.10	5.02 (2)	28.53 (2)	1.4×10^{-1}	log $K_{ML} = 11.75$ (1), log $K_{MHL} = 2.92$ (1)	337
$[Co(TAOTD)]^{2+}$	25	0.10	2.20 (3)	21.14 (3)	2.1×10^{-4}	log $K_{ML} = 9.47$ (2), log $K_{MHL} = 6.20$ (3)	337
$[Co(PXBDE)(EN)]^{2+}$	25	0.10	9.58		5.1×10^{3}		357
$[Co(PXBDE)(GLY)]^{+}$	25	0.10	6.95		1.2×10^{1}		357
[Co(PYEN)]	25	0.10	5.99		1.3		338
[Co(PABNDT)]	35	0.20	9.64	37.56		log $K_{ML} = 13.96$	380
				II. μ-Peroxo-μ-Hydroxo-Dibridged Products[q,r]			
$[Co(EN)_2]^{2+}$	25	0.10				log $K_{O_2} = 24.9\ (2)^s$	347
	25	0.10	10.8		8.5×10^{14}		581
	25	1.0				$\Delta G^\circ = -14.8$ (4) kcal mol^{-1}, $\Delta H^\circ = -29.4$ (6) kcal mol^{-1}, $\Delta S^\circ = -40$ (4) cal deg^{-1} mol^{-1}	343
$[Co(HEDIEN)]^{2+}$	25	0.10	1.5		4.3×10^{5}		581
$[Co(DIEN)]^{2+}$	25	0.10				log $K_{O_2} = 14.6\ (2)^t$	347
	25	0.10	1.1		1.7×10^{5}		581
			8.2				409
	see footnote u						351
$[Co(DIEN)(OH)]^{2+}$	25	0.10	1.4 (1)		3.4×10^{5}		351
$[Co(TRIEN)]^{2+}$	25	0.10		10.4 (1)		log $K_{ML} = 10.4\ (0.1)^v$	350
	25	0.10	6.1		1.7×10^{10}		581
$[Co(TREN)]^{2+}$	25	0.10				log $K_{O_2} = 26.92$ (3),[t] $\Delta G^\circ = -13.5$ (1) kcal mol^{-1}, $\Delta H^\circ = -63$ (10) kcal mol^{-1}, $\Delta S^\circ = -100$ (15) cal deg^{-1} mol^{-1}	362
							362
	25	0.10	4.4		3.4×10^{8}		362
[Co(UEDDA)]	25	0.10	−5.3 (1)		6.8×10^{-2}		350, 581
[Co(SEDDA)]	25	0.10	−4.24 (6)		7.8×10^{-1}		350, 581
$[Co(UDTMA)]^{+}$	25	0.10	2.4		3.4×10^{6}		581
	25	0.10	2.35 (2)		3.0×10^{6}	log $K_{O_2} = 23.54\ (4)^w$	393
$[Co(SDTMA)]^{+}$	25	0.10	2.3		2.7×10^{6}		581
	25	0.10	2.39 (2)		3.3×10^{6}	log $K_{O_2} = 23.71\ (4)^w$	393
$[Co(BPY)]^{2+}$	25	0.10	−2.6		3.4×10^{1}	log $K_{OH} = -6.8^x$	354
$[Co(PHEN)_2]^{2+}$	25	0.10	see footnote y				354
	25	0.10	−2.72 (12)		2.6×10^{1}	log $K_{OH} = -7.25\ (40)^z$	344
	25	0.10	−2.94 (10)		1.5×10^{1}		344
$[Co(PHEN)GLY)]^{+}$	25	0.10	−2.51		4.2×10^{1}	log $K_{OH} = -6.15^z$	587
$[Co(PHEN)(ALA)]^{+}$	25	0.10	−1.97		1.4×10^{2}	log $K_{OH} = -5.86^z$	587
$[Co(PHEN)(ABA)]^{+}$	25	0.10	−2.39		5.5×10^{1}	log $K_{OH} = -6.35^z$	587
$[Co(PHEN)(n\text{-VAL})]^{+}$	25	0.10	−2.37		5.8×10^{1}	log $K_{OH} = -6.41^z$	587

TABLE XXXIII. (*Continued*)

complex	T, °C	μ, M	log K_{O_2}[a]	log K_{O_2}'[b]	$P_{1/2}^{-1}$,[c] atm^{-1}	other constants	ref
[Co(PHEN)(*n*-LEU)]$^+$	25	0.10	−1.82		2.0×10^2	log $K_{OH} = -5.87$[z]	587
[Co(IMEN)]$^{2+}$	25	0.20	4.3[aa]			pK(CoL)$_2$O$_2$(OH) = 17.9 potentiometric, 18.3 polarographic[ab]	365
[Co(GLY)$_2$]	25	0.10	see footnote *l*				151
[Co(ALA)$_2$]	25	0.10	−4.03 (3)		1.3		151
[Co(PRO)$_2$]	25	0.10	−4.41 (1)		5.3×10^{-1}		151
[Co(LEU)$_2$]	25	0.10	−4.01 (1)		1.3		151
[Co(VAL)$_2$]	25	0.10	−3.8 (2)		2.1		151
[Co(HISHIS)]$^+$	25	0.10				log $K_{O_2} = -8.2$ (2),[ac] log $K_{O_2}' = 7.3$[ad]	316
[Co(GLYHIS)]$^+$	25	0.10				log $K_{O_2} = -13.5$ (2),[ac] log $K_{O_2}' = 1.0$[ad]	316
[Co(HISGLY)]$^+$	25	0.10				log $K_{O_2} = -16.6$ (2),[ac] log $K_{O_2}' = -2.3$[ad]	316
[Co(Glycylhistamine)]$^{2+}$	25	0.10				log $K_{O_2} = -15.5$ (1),[ac] log $K_{O_2}' = 0.4$[ad]	316
[Co(GLYASP)]$^+$	25	0.10				log $K_{O_2} = -20.1$ (1),[ac] log $K_{O_2}' = -1.6$[ad]	316
[Co(ASPGLY)]$^+$	25	0.10				log $K_{O_2} = -20.7$ (2)[ac]	316
[Co(histamine)]$^{2+}$			8.5				409
	25	0.13				$\Delta G° = -11.55$ (7) kcal mol^{-1}	334
[Co(TRIEN)]$^{2+}$	35	0.20	6.9 (1)	28.1 (7)		$K_{ML} = 4.3$ (6) $\times 10^{10}$	345
[Co(TAOD)]$^{2+}$	35	0.20	0.8 (1)	28.4 (7)		$K_{ML} = 6.2$ (1) $\times 10^{13}$	345
[Co(TACT)]$^{2+}$	35	0.20	1.2 (1)	29.8 (1)		$K_{ML} = 1.9$ (3) $\times 10^{14}$	345
[Co(7-TACTD)]$^{2+}$	35	0.20	dec			$K_{ML} = 8.2$ (1.2) $\times 10^{10}$	345
[Co(PXTREN)]$^{2+}$	25	0.10	3.69		6.6×10^7		338
[Co(BISTREN)]$^{2+}$	25	0.10	−2.58		3.7×10^1		359
[Co(BISDIEN)]$^{2+}$	25	0.10	−0.42		5.1×10^3		360
[Co(PYEN)]$^{2+}$	25	0.10	3.83		9.1×10^7		348
[Co(PYDE)]$^{2+}$	25	0.10	6.26		2.5×10^{10}		338
B. Equilibrium Constants for Reaction of Ni(II) and Fe(II) Complexes with O_2 in Aqueous Solution							
[Ni(DTAHD)]	35	0.2	4.26[af]		~2.5		385
[Fe(PABNDT)]	35	0.2	7.94[ag]	29.48[ah]	$\sim 1.2 \times 10^2$	log $K_{ML} = 10.76$	380

C. Equilibrium Constants for Reaction of O_2 Gas with Solid-State Ferrous, Cobaltous, and Manganous Complexes

complex	T, °C	K_{O_2},[ai] torr^{-1}	$P_{1/2}$, torr	$P_{1/2}^{-1}$,[c] atm^{-1}	other constants	ref
[Co(SALEN)]	25	~0.2	~5	1.52×10^2		116
	0	>0.2	<5	1.52×10^2		116
	25	0.02	50[aj]	1.52×10^1	$\Delta H° = 19.1$ kcal (mol of O_2)$^{-1}$, $\Delta G° = 1.6$ kcal (mol of O_2)$^{-1}$, $\Delta S° = 59$ eu	120
	0	~0.2	~5[aj]	1.52×10^2		120
[Co(3-FSALEN)]	25	~0.5	~2	3.8×10^2		116
	0	~2.5	~0.4	1.9×10^3		116
[Co(3-MeOSALEN)]	25	0.015	66[aj]	1.2×10^1	$\Delta H° = 19.1$ kcal (mol of O_2)$^{-1}$, $\Delta G° = 1.45$ kcal (mol of O_2)$^{-1}$, $\Delta S° = 59$ eu	120
[Co(3-NO$_2$SALEN)]	25	0.029	35[aj]	2.2×10^1	$\Delta G° = 2.0$ kcal (mol of O_2)$^{-1}$	
[Co(3-EtOSALEN)]	25	0.5	2[aj]	3.8×10^2	$\Delta H° = 18.9$ kcal (mol of O_2)$^{-1}$, $\Delta G° = 3.5$ kcal (mol of O_2)$^{-1}$, $\Delta S° = 52$ eu	120
	0	1.4	0.7[aj]	1.1×10^3		120

[Fe(TPP)(PImSG)]	−127	2.5	~0.4	1.9×10^3		93, 433
	−78	0.25	~4.0	1.9×10^2		93, 433
	0	0.0043	~230	3.3		93, 433
[Fe(TPivPP)(*N*-MeIm)]	20	3.2	0.31	2.5×10^3	$\Delta H° = -15.6$ (2) kcal mol^{-1}, $\Delta S° = -38$ (1) cal deg^{-1} mol^{-1}, $K_{O_2} = 2400$ atm^{-1}	313
[Co(TPivPP)(*N*-MeIm)]	25	0.016	61	1.2×10^1	$\Delta H° = -13.3$ (9) kcal mol^{-1}, $\Delta S° = -40$ (3) eu[w]	314
	15	0.0034	29[ak]	2.6×10^1		314
[Mn(Me_2PPh)Br_2]	25[d]	0.33	~3	2.5×10^2		57
[Mn(Et_2PPh)Br_2]	25[d]	0.029	~35	2.2×10^1		57
[Mn(Bu_3P)$(NCS)_2$]	25[d]	0.0083	~120	6.3		57

D. Equilibrium Constants for Reactions of Ferrous and Manganous Complexes with O_2 in Organic Solvents

complex	T, °C	solvent	log K_{O_2},[al] torr^{-1}	$P_{1/2}$, torr	$P_{1/2}^{-1}$,[c] atm^{-1}	other constants	ref
[Fe(DCC-CH_3)(*m*-xylyl)(PYR)]$^{2+}$	−41.5	acetone/PYR/H_2O (3:1:1)	0.16 (1)	6.3	120		381
[Fe(DCC-CH_3)(*m*-xylyl)(Cl)]$^{2+}$	−41.5	acetone/PYR (4:1)	0.015 (3)	67	11		381
[Fe(DCC-CH_3)(*m*-xylyl)(PYR)]$^{2+}$	−41.5	acetone/PYR (4:1)	0.08 (1)	13	61		381
[Fe(DCC-CH_3)(*m*-xylyl)(*N*-MeIm)]$^{2+}$	−41.5	acetone/*N*-MeIm (4:1)	1.7 (2)	0.59	1300		381
[FeCu-4(*N*-MeIm)]	21 (1)	benzene	31	0.032	2.4×10^4		382
[FeCu-5(THPIm)]	21 (1)	benzene	5	0.2	3.8×10^3		382
[FeSP-15(DCHIm)]	21 (1)	benzene	15	0.067	1.1×10^4		382
[Fe(TPP)$(PYR)_2$]$^{2+}$	−79	CH_2Cl_2				$K_{O_2} = 0.71$ (5)[am]	424
[Fe(TPP)$(PIP)_2$]$^{2+}$	−79	CH_2Cl_2				$K_{O_2} = 56.0$ (8.0)[am]	424
[Fe(TPP)(*N*-MeIm)$_2$]$^{2+}$	−79	CH_2Cl_2				$K_{O_2} = 5.4$ (9)[am]	424
[Fe(TPivPP)(Me_2Im)]$^{2+}$	25	toluene	0.026	38[ak]	2.0×10^1	$\Delta H° = -14.3$ (5) kcal mol^{-1}, $\Delta S° = -42$ (2)[w]	425
[Fe(Piv_3(4ClmP)P]$^{2+}$	25	toluene	1.7	0.60[ak]	1.3×10^3	$\Delta H° = -16.8$ (5) kcal mol^{-1}, $\Delta S° = -42$ (2)[w]	425
[Fe(Piv_3(5ClmP)P)]$^{2+}$	25	toluene	1.7	0.58[ak]	1.3×10^3	$\Delta H° = -16.3$ (8) kcal mol^{-1}, $\Delta S° = -40$ (3)[w]	425
[Fe(MPIXDME)(BzIm)]$^{2+}$	−45	DMF	0.013	~80	9.5		426
[Fe(MPIX-IPA)]$^{2+}$	−45	DMF	>1	<1	7.2×10^2		426
[Fe(PYP-IPA)]$^{2+}$	−45	CH_2Cl_2	5	0.2	3.8×10^3		427
[Fe(MP-MPP)]$^{2+}$	−45	CH_2Cl_2	≪0.0013	≫760[an]	1		427
[Fe(PYP-IPA)]$^{2+}$	22	CH_2Cl_2	5.2[ao]				428
	22	$HCON(CH_3)_2$	5.7[ao]				428
	22	$HCON(CH_3)_2/H_2O$	6[ao]				428
	22	H_2O[ap]	6.2[ao]		2.3×10^3		428
[Fe(PYP-PP)]$^{2+}$	22	$HCON(CH_3)_2$	4.3[ao]				428
	22	$HCON(CH_3)_2/H_2O$	4.7[ao]				428
	22	H_2O[ap]	5[ao]		1.2×10^2		428
	22	toluene	3[ao]				428
[Fe(PYP-PP)][26]	−45	DMF	0.2	5	1.5×10^2		429
	−45	*bj*	0.036	28	27		429
	−45	toluene	0.025	400	1.9		429
[Mn(TPP)]	−78	toluene	~2.1	0.48	1.6×10^3		386
[Mn(TPP)(4-CNPYR)]	−78	toluene			$-\log K = 5.57$[am]		386
[Mn(TPP)/(PYR)]	−78	toluene				$-\log K = 5.96$[am]	386
[Mn(TPP)(3,4-LUT)]	−78	toluene				$-\log K = 7.14$[am]	386
[Mn(TPP)(*N*-MeIm)]	−78	toluene				$-\log K = 7.97$[am]	386
[Mn(TPP)(*s*-BuNH_2)]	−78	toluene				$-\log K = 7.36$[am]	386
[Mn(TPP)((*n*-Bu)$_3$P)]	−78	toluene				$-\log K = 8.48$[am]	386
[Mn(TPP)((EtO_3)P)]	−78	toluene				$-\log K = 5.51$[am]	386
[Mn(TPP)(thioanisole)]	−78	toluene				$-\log K = 7.45$[am]	386

TABLE XXXIII. (*Continued*)

E. Thermodynamic Parameters for the Addition of O_2 to $[M(2\text{-}PHOS)_2][B(C_6H_4)_4]$ in Chlorobenzene at 25 °C

metal	ΔH°_2*,[aq] kcal mol^{-1}	ΔS°_2*,[aq] eu	ΔG°_2*,[aq] kcal mol^{-1}	ref
Co	3.4 (3)	−28 (4)	10.3	387
Rh	11.6 (3)	−24 (4)	18.8	387
	23.5 (3)[ar]	4 (4)[ar]		387
	−11.9 (3)[as]	−28 (4)[as]		387
Ir	6.5 (3)	−38 (4)	17.8	387

F. Equilibrium Constants for Reaction of Cobaltous Complexes with O_2 in Organic Solvents

complex	T, °C	solvent	log K_{O_2},[at] torr^{-1}	$P_{1/2}$, torr	$P_{1/2}^{-1}$,[c] atm	other constants	ref
[Co(SALEN)]	20.0	Me_2SO	−2.51	324	2.35	ΔH° = −16 (2) kcal mol^{-1}, ΔS° = −67 (3) eu[au]	395
	25.8	Me_2SO	2.64	437	1.74		395
	35.1	Me_2SO	−3.11	1.29×10^3	0.590		395
	20.0	PYR	−1.05	11.2	67.7	ΔG° = 1.4 kcal mol^{-1}, ΔH° = −12.4 kcal mol^{-1}, ΔS° = −37 eu	396
	20.0	DMF				K_T = 64.0 dm^6 mol^{-2},[av] ΔH°_T = −59 kJ mol^{-1}, ΔS°_T = −142 J K^{-1} mol^{-1} [aw]	397
	20.0	PYR				K_{O_2} = 10^4 dm^3 mol^{-1}, ΔH° = −52 kJ mol^{-1}, ΔS° = −96 J K^{-1} mol^{-1} [aw]	397
	20.0	PYR[at]				K_T = 10^5 dm^6 mol^{-2},[av] ΔH°_T = −85 kJ mol^{-1}, ΔS° = −184 J K^{-1} mol^{-1} [aw]	397
[Co(SAL(±)DPEN)]	20.0	DMF				K_T = 73 dm^6 mol^{-2},[av] ΔH°_T = −63 kJ mol^{-1}, ΔS°_T = −193 J K^{-1} mol^{-1} [aw]	397
	20.0	PYR				K_{O_2} = 25 dm^3 mol^{-1},[at] ΔH° = −43 kJ mol^{-1}, ΔS° = −121 J K^{-1} mol^{-1} [aw]	397
	20.0	PYR[ax]				K_T = 85 dm^6 mol^{-2},[av] ΔH° = 83 kJ mol^{-1}, ΔS° = −239 J K^{-1} mol^{-1} [aw]	397
[Co(SAL(m)DPEN)]	20.0	DMF				K_T = 923 dm^6 mol^{-2},[av,ay] ΔH° = −63 kJ mol^{-1}, ΔS° = −159 J K^{-1} mol^{-1} [aw]	397
	20.0	PYR				K_{O_2} = 1000 dm^3 mol^{-1},[at] ΔH° = −72 kJ mol^{-1}, ΔS° = −188 J K^{-1} mol^{-1} [aw]	397
	20.0	PYR[ax]				K_T = 3700 dm^6 mol^{-2},[av] ΔH° = −107 kJ mol^{-1}, ΔS° = −322 J K^{-1} mol^{-1} [aw]	397
[Co(SAL(±)CHXN)]	20.0	DMF				K_T = 307 dm^6 mol^{-2},[av,ay] ΔH° = −59 kJ mol^{-1}, ΔS° = −155 J K^{-1} mol^{-1} [aw]	397
	20.0	PYR				K_{O_2} = 231 dm^3 mol^{-1},[at] ΔH° = −54 kJ mol^{-1}, ΔS° = −138 J K^{-1} mol^{-1} [aw]	397
	20.0	PYR[ax]				K_T = 2300 dm^6 mol^{-1},[av] ΔH° = −81 kJ mol^{-1}, ΔS° = −209 J K^{-1} mol^{-1} [aw]	397
[Co(SAL(m)CHXN)]	20.0	DMF				K_T = 400 dm^6 mol^{-2},[av] ΔH° = −59 kJ mol^{-1}, ΔS° = −151 J K^{-1} mol^{-1} [aw]	
	20.0	PYR				K_{O_2} = 95 dm^3 mol^{-1},[at] ΔH° = −59 kJ mol^{-1}, ΔS° = −168 J K^{-1} mol^{-1} [aw]	397
	20.0	PYR				K_T = 540 dm^6 mol^{-2}, ΔH° = −89 kJ mol^{-1}, ΔS° = −255 J K^{-1} mol^{-1}	397
[Co(SAL(±)BN)]	20.0	DMF				$K_T \cong$ 150 dm^6 mol^{-2} [av]	397
[Co(SAL(m)BN)]	20.0	DMF				$K_T \cong 10^3$ dm^6 mol^{-2}	397
[Co(ACACEN)DMF]	−10.0	DMF				log K_{O_2} = 2.11 (10)	248, 398
[Co(ACACEN)PYR]	20.0	PYR		2.75	276	K_{O_2} = 6.6 × 10^4 M^{-1},[az] ΔG = −6.45 kcal mol^{-1}, ΔH = −15.0 (1.35) kcal mol^{-1}	139
						ΔS° = −29 eu	139

	0	toluene	−2.08 (3)	120	6.32	$\Delta H^\circ = -17.3$ (5) kcal mol^{-1}, $\Delta S^\circ = -72.7$ eu	394
	−10	toluene	−1.53 (2)	33.9	22.4		394
	−15	toluene	−1.31 (3)	20.4	37.2		394
	−21	toluene	−0.90 (2)	0.13	6.0×10^3		394
	−31	toluene	−0.28	1.9	4.0×10^2		399
[Co(PHACACEN)PYR]	−10	toluene	−2.12 (2)	132	5.77	$\Delta H^\circ = -16.3$ (6) kcal mol^{-1}, $\Delta S^\circ = -72.5$ (2.5) eu	394
	−20.5	toluene	−1.54 (3)	34.7	21.9		394
	−31	toluene	−0.89 (3)	7.8	98		394, 399
	−37.4	toluene	−0.58 (2)	3.8	2.0×10^2		394
[Co(MEACACEN)PYR]	−21	toluene	−1.74	55.0	13.8	$\Delta H^\circ = -15.6$ (1.5) kcal mol^{-1}, $\Delta S^\circ = -69.5$ (5.0) eu	394
	−31	toluene	−1.12 (3)	13.2	57.7		394, 399
	−37.4	toluene	−0.79 (2)	6.2	1.23×10^2		394
[Co(BENACEN)PYR]	−21	toluene	−2.03 (3)	107	7.09	$\Delta H^\circ = -16.6$ (8) kcal mol^{-1}, $\Delta S^\circ = -75.1$ (2.6) eu	394
	−31	toluene	−1.38 (2)	24.0	31.7		394, 399
	−37.4	toluene	1.06 (4)	11.5	66.2		394
[Co(BENACEN)-*n*-BuNH$_2$]	0	toluene	−1.93 (4)	85.1	8.93	$\Delta H^\circ = -17.4$ (7) kcal mol^{-1}, $\Delta S^\circ = -72.3$ (2.5) eu	394
	−10	toluene	−1.34 (3)	21.9	34.7		394
	−21	toluene	−0.75 (2)	5.6	1.35×10^2		394
[Co(BENACEN)-*i*-BuNH$_2$]	0	toluene	−1.95 (4)	89.1	8.53	$\Delta H^\circ = -18.0$ (7) kcal mol^{-1}, $\Delta S^\circ = -80.0$ (3.0) eu	394
	−10	toluene	−1.50 (5)	31.6	24.0		394
	−21	toluene	−0.74 (3)	5.50	1.38×10^2		394
[Co(BENACEN)*N*-MeIm]	0	toluene	−2.00 (4)	100	7.60	$\Delta H^\circ = -17.5$ (5) kcal mol^{-1}, $\Delta S^\circ = -73.5$ (2.0) eu	394
	−10	toluene	−1.55 (3)	35.5	21.4		394
	−15	toluene	−1.18 (3)	15.1	50.2		394
	−21	toluene	−0.82 (2)	6.6	1.15×10^2		394
[Co(BENACEN)5-Cl-*N*-MeIm]	−10	toluene	−1.64 (4)	43.7	17.4	$\Delta H^\circ = -17.5$ (6) kcal mol^{-1}, $\Delta S^\circ = -74.5$ (1.8) eu	394
	−15	toluene	−1.38 (3)	24.0	31.7		394
	−21	toluene	−0.99 (3)	9.8	77.8		394
[Co(BENACEN)BuNH$_2$]	0	toluene	−2.38 (3)	240	3.17	$\Delta H^\circ = -17.8$ (9) kcal mol^{-1}, $\Delta S^\circ = -76.1$ (3.0) eu	394
	−10	toluene	−1.90 (3)	79.4	9.57		394
	−21	toluene	−1.18 (2)	15.1	50.2		394
[Co(BENACEN)PIP]	−10	toluene	−1.86 (3)	72.4	10.5	$\Delta H^\circ = -16.7$ (7) kcal mol^{-1}, $\Delta S^\circ = -71.9$ (2.4) eu	394
	−15	toluene	−1.57 (2)	37.2	20.5		394
	−21	toluene	−1.23 (3)	17.0	44.8		394
[Co(BENACEN)3,4-LUT]	−15	toluene	−1.89 (1)	77.6	9.79	$\Delta H^\circ = -16.8$ (9) kcal mol^{-1}, $\Delta S^\circ = -73.9$ (2.8) eu	394
	−21	toluene	−1.66 (2)	45.7	16.6		394
	−31	toluene	−0.99 (4)	9.8	78		394
[Co(BENACEN)4-CNPYR]	−21	toluene	−2.68 (6)	479	1.59	$\Delta H^\circ = -16.9$ (7) kcal mol^{-1}, $\Delta S^\circ = -77.2$ (2.5) eu	394
	−31	toluene	−2.15 (5)	141	5.38		394
	−37.4	toluene	−1.68 (4)	47.9	15.9		394
[Co(BENACEN)PPh$_3$]	−37.4	toluene	−2.41 (5)	257	2.96		394
[Co(BENACEN)CH$_3$CH$_2$SCH$_3$]	−51.5	toluene	−2.01 (4)	102	7.43		394
[Co(SACSACEN)PYR]	−31	toluene	−2.12 (2)	132	5.77		394, 399
	−45	toluene	−1.43 (2)	26.9	28.2	$\Delta H^\circ = -13.3$ (5) kcal mol^{-1}, $\Delta S^\circ = -64.5$ (2.3) eu	394
	−51.5	toluene	−0.98 (2)	9.5	76		394
[Co(SACSACEN)PYR][ba]	−45	toluene	−1.95 (3)	89.1	8.53	$\Delta H^\circ = -12.0$ (3) kcal mol^{-1}, $\Delta S^\circ = -6.15$ (1.2) eu	315
	−51.5	toluene	−1.60 (3)	39.8	19.1		315
	−63.5	toluene	−0.93 (2)	8.5	89		315
[Co(SACSACEN)DMF][ba]	−45	toluene	−2.08 (2)	120	6.32	$\Delta H^\circ = -14.1$ (4) kcal mol^{-1}, $\Delta S^\circ = -71.3$ (1.4) eu	315
	−51.5	toluene	−1.73 (3)	53.7	14.2		315
	−57	toluene	−1.31 (3)	20.4	37.2		315
	−63.5	toluene	−0.90 (2)	7.9	96		316

TABLE XXXIII. (*Continued*)

complex	T, °C	solvent	log K_{O_2},[at] torr^{-1}	$P_{1/2}$, torr	$P_{1/2}^{-1}$,[c] atm	other constants	ref
[Co(SACSACEN)MeIm][ba]	−37.4	toluene	−2.10 (3)	126	6.04	ΔH° = −15.4 (6) kcal mol^{-1}, ΔS° = −75.0 (2.3) eu	315
	−45	toluene	−1.59 (3)	38.9	19.5		315
	−51.5	toluene	−1.19 (3)	15.5	49.1		315
	−30.8	DMF	−2.00 (2)	100	7.6	ΔH° = −16.1 (6) kcal mol^{-1}, ΔS° = −75.6 (2.1) eu	315
	−37.4	DMF	−1.60 (2)	39.8	19.1		315
	−45	DMF	−1.12 (2)	13.2	57.7		315
	−51.5	DMF	−0.72 (5)	5.2	1.4 × 10^2		315
	−15.9	CH_3CN	−1.97 (3)	93.3	8.14	ΔH° = −18.5 (1.7) kcal mol^{-1}, ΔS° = −80.9 (6.0) eu	315
	−23.0	CH_3CN	−1.55	35.5	21.4		315
	−30.8	CH_3CN	−1.00 (2)	10	76		315
[Co(BENACEN)PYR]	0	toluene	−2.25 (2)	178	4.27	ΔH°_{20} = −16.2 (3) kcal mol^{-1}, ΔS°_{20} = −69.6 (1.2) eu	315
	−7	toluene	−1.90 (2)	79.4	9.57		315
	−15.9	toluene	−1.45 (3)	28.2	27.0		315
	−23	toluene	−1.05 (2)	11.2	67.7		315
[Co(CH_3OBENACEN)PYR][ba]	0	toluene	−2.22 (4)	166	4.58	ΔH°_{20} = −16.5 (4) kcal mol^{-1}, ΔS°_{20} = −70.6 (1.4) eu	315
	−7	toluene	−1.88 (1)	75.9	10.0		315
	−15.9	toluene	−1.39 (2)	24.5	31.0		315
	−23	toluene	−1.01 (3)	10.2	74.3		315
[Co(CH_2BENACEN)PYR][ba,bb]	0	toluene	−2.20 (2)	158	4.80	ΔH°_{20} = −16.3 (8) kcal mol^{-1}, ΔS°_{20} = −69.8 (2.8) eu	315
[Co(BrBENACEN)PYR][ba,bb]	0	toluene	−2.12 (1)	132	5.77	ΔH°_{20} = −17.1 (4) kcal mol^{-1}, ΔS°_{20} = −72.4 (1.6) eu	315
[Co(ClBENACEN)PYR][ba,bb]	0	toluene	−2.05 (2)	112	6.77	ΔH°_{20} = −17.3 (7) kcal mol^{-1}, ΔS°_{20} = −72.8 (2.6) eu	315
[Co(BENSACEN)PYR][ba]	−45	toluene	−2.47 (3)	295	2.58		315
	−51.5	toluene	−2.22 (2)	166	4.58	ΔH°_{20} = −8.05 (30) kcal mol^{-1}, ΔS°_{20} = −46.5 (1.2) eu	315
	−63.5	toluene	−1.78 (2)	60.3	12.6		315
[Co(CH_3OBENSACEN)PYR]	−37.4	toluene	−2.62 (2)	417	1.82	ΔH°_{20} = −10.8 (6) kcal mol^{-1}, ΔS°_{20} = −57.6 (2.3) eu	315
	−45	toluene	−2.22 (3)	166	4.58		315
	−51.5	toluene	−2.08 (4)	120	6.32		315
	−63.5	toluene	−1.34 (2)	21.9	34.7		315
[Co(CH_3BENSACEN)PYR][ba,bb]	−37.4	toluene	−2.26 (3)	182	4.18	ΔH°_{20} = −11.2 (3) kcal mol^{-1}, ΔS°_{20} = −57.8 (1.0) eu	315
[Co(BrBENSACEN)PYR][ba,bb]	−37.4	toluene	−2.18 (3)	151	5.02	ΔH°_{20} = −12.1 (4) kcal mol^{-1}, ΔS°_{20} = −61.1 (1.3) eu	315
[Co(ClBENSACEN)PYR][ba,bb]	−37.4	toluene	−2.19 (3)	155	4.91	ΔH°_{20} = −13.3 (4) kcal mol^{-1}, ΔS°_{20} = −66.3 (1.6) eu	315
[Co(TACTD)][ba]	−50	MeOH	−3.69[bc]	4.90 × 10^3	0.155		399
[Co(HMTACTD)]$^{2+}$ [ba,bb]	−62	DMF	−1.81[bd]	64.5	11.8		400
	−49	DMF	−2.3[bd]	200	3.7		400
	−37	DMF	−2.81[bd]	645	1.18		400
[Co(*p*-MeTPP)PYR][ba,bb]	−56.5	DMF	2.78[be]				366
[Co(*p*-FTPP)PYR][ba,bb]	−56.5	DMF	2.23[be]				366
[Co(*p*-ClTPP)PYR][ba,bb]	−56.5	DMF	2.21[be]				366
[Co(*p*-CNTPP)PYR][ba,bb]	−56.5	DMF	2.06[be]				366
[Co(*p*-O_2TPP)PYR][bb]	−56.5	toluene	−0.093 (12)				366
[Co(*p*-NO_2TPP)PYR]	−72	toluene	2.66[be]				366
[Co(*p*-MeOTPP)PYR]	−56.5	toluene	2.38[be]				366
	−65	toluene	2.84 (3)[be]			ΔG° = 2.34 (3) kcal mol^{-1}, ΔH° = −9.3 (1.1) kcal mol^{-1}, ΔS° = −55 cal deg^{-1} mol^{-1}	145
[Co(*p*-MeOTPP)4-PIC]	−65	toluene	2.95 (3)[be]			ΔG° = 2.09 (3) kcal mol^{-1}, ΔH° = −8.8 (9) kcal mol^{-1}, ΔS° = −52 cal deg^{-1} mol^{-1}	145
[Co(*p*-MeOTPP)3,4-LUT]	−65	toluene	2.81 (3)[be]			ΔG° = 2.23 (3) kcal mol^{-1}, ΔH° = −9.2 (1) kcal mol^{-1}, ΔS° = −54 cal deg^{-1} mol^{-1}	145

	−65	toluene				$K_4 = 730$,[bf] $\Delta H°_4 = -7.4$ (1.0) kcal mol^{-1}, $\Delta S° = -23$ cal deg^{-1} mol^{-1} [be]	145
[Co(*p*-MeOTPP)4-DMAP]	−65	toluene	3.41 (3)[be]			$\Delta G° = 1.79$ (3) kcal mol^{-1}, $\Delta H° = -8.5$ (8) kcal mol^{-1}, $\Delta S° = -48$ cal deg^{-1} mol^{-1}	145
[Co(*p*-MeOTPP)γ-Coll]	−65	toluene	2.41 (3)[be]			$\Delta G° = 2.75$ (3) kcal mol^{-1}, $\Delta H° = -9.5$ (1.3) kcal mol^{-1}, $\Delta S° = -58$ cal deg^{-1} mol^{-1}	145
[Co(*p*-MeOTPP)5-Cl-*N*-MeIm]	−65	toluene	2.10 (3)[be]			$\Delta G° = 3.04$ (3) kcal mol^{-1}, $\Delta H° = -8.6$ (1) kcal mol^{-1}, $\Delta S° = -54$ cal deg^{-1} mol^{-1}	145
[Co(*p*-MeOTPP)*N*-MeIm]	−65	toluene	3.58 (3)[be]			$\Delta G° = 2.63$ (3) kcal mol^{-1}, $\Delta H° = -8.9$ (5) kcal mol^{-1}, $\Delta S° = -49$ cal deg^{-1} mol^{-1}	145
[Co(*p*-MeOTPP)PIP]	−65	toluene	2.87 (3)[be]			$\Delta G° = 2.17$ (3) kcal mol^{-1}, $\Delta H° = -8.2$ (1) kcal mol^{-1}, $\Delta S° = -49$ cal deg^{-1} mol^{-1}	145
	−65	toluene				$K_4 = 210$,[bf] $\Delta H_4 = -6.7$ (1.0) kcal mol^{-1}, $\Delta S = -21$ cal deg^{-1} mol^{-1}	145
[Co(*p*-MeOTPP)PYR]	−65	CS_2	−2.18 (3)	151	5.02	$\Delta G° = 2.08$ (3) kcal mol^{-1}, $\Delta H° = -8.5$ (5) kcal mol^{-1}, $\Delta S° = -51$ cal deg^{-1} mol^{-1} [be]	145
[Co(*p*-MeOTPP)3,4-LUT]	−65	CS_2	−2.10 (3)	126	6.04	$\Delta G° = 2.00$ (3) kcal mol^{-1}, $\Delta H° = -9.0$ (6) kcal mol^{-1}, $\Delta S° = -53$ cal deg^{-1} mol^{-1}	145
[Co(TPP)3-MePYR]	−63	CH_2Cl_2	−1.67 (11)	46.8	16.2		145
	−53	CH_2Cl_2	−2.13 (8)	135	5.63	$\Delta G°_{298} = 5.7$ kcal mol^{-1}, $\Delta H° = 8.1$ kcal mol^{-1},[bg] $\Delta S° = -46$ eu[bh]	145
	−45	CH_2Cl_2	−2.31 (10)	204	3.72		401
[Co(TPP-AABl)]	−63	CH_2Cl_2	−1.28 (11)	19.1	39.9		401
	−53	CH_2Cl_2	−1.69 (9)	49.0	15.5	$\Delta G°_{298} = 4.7$ kcal mol^{-1}, $\Delta H° = -7.2$ kcal mol^{-1},[bg] $\Delta S° = -40$ eu[bh]	401
	−45	CH_2Cl_2	−1.85 (11)	70.8	10.7		401
	−78	toluene	−1.82 (5)	66.1	11.5		401
	−63	toluene	−2.19 (10)	155	4.91	$\Delta G°_{298} = 5.1$ kcal mol^{-1}, $\Delta H° = -5.0$ kcal mol^{-1},[bg] $\Delta S° = -34$ eu[bh]	401
	−53	toluene	−2.49 (10)	309	2.46		401
[Co(TPP-AAB_2)]	−78	CH_2Cl_2	−1.14 (11)	13.8	55.1		401
	−63	CH_2Cl_2	−1.84 (5)	69.2	11.0	$\Delta G°_{298} = 6.1$ kcal mol^{-1}, $\Delta H° = -8.5$ kcal mol^{-1},[bg] $\Delta S° = -49$ eu[bh]	401
	−56	CH_2Cl_2	−2.11 (6)	129	5.90		401
[Co(TPivPP)*N*-MeIm]	25	toluene	−2.15	140[ak]	5.43	$\Delta H° = -12.2$ (3) kcal mol^{-1}, $\Delta S° = -38$ (1) eu[w]	425
	15	toluene	−1.85	70[ak]	11		425
[Co(TPivPP)Me_2Im]	25	toluene	−2.95	900[ak]	0.844	$\Delta H° = -11.8$ (4) kcal mol^{-1}, $\Delta S° = -40$ (2) eu[w]	425
	15	toluene	−2.65	450[ak]	1.69		425
[Co(PPIXDME)PYR]	−37	CH_2Cl_2	−1.55 (10)	35.5	21.4	$\Delta G°_{298} = 5.0$ kcal mol^{-1}, $\Delta H° = -12.0$ kcal mol^{-1},[bg] $\Delta S = -57$ eu[bh]	401
	−45	toluene	−2.84 (6)	692	1.10		421, 402
	−57.5	toluene	−2.25 (6)	178	4.27	$\Delta H° = -9.2$ kcal mol^{-1}, $\Delta S° = -53$ eu	421, 402
	−63.5	toluene	−2.09 (6)	123	6.18		421, 402
	−43.5	toluene	−2.60 (7)	398	1.91	$\Delta G° = 2.73$ kcal mol^{-1}, $\Delta H° = -10.3$ kcal mol^{-1}, $\Delta S° = -55$ eu	403
	−49.0	toluene	−2.32 (6)	209	3.64	$\Delta G° = 2.37$ kcal mol^{-1}	403
	−53.5	toluene	−2.10 (3)	126	6.04	$\Delta G° = 2.10$ kcal mol^{-1}	403
	−59.0	toluene	−1.89 (2)	77.6	9.79	$\Delta G° = 1.85$ kcal mol^{-1}	403
[Co(PPIXDME)PYR][bb]	−15.5	DMF	−2.60 (8)	398	1.91	$\Delta G° = 3.06$ kcal mol^{-1}, $\Delta H° = -14.5$ kcal mol^{-1}, $\Delta S° = -66$ eu	403
[Co(PPIXDME)DMF]	−23	DMF	−1.6	40	19		404
	−31	toluene	−2.88 (6)	759	1.00	$\Delta H° = -11.0$ kcal mol^{-1}, $\Delta S° = -59$ eu	421
	−45	toluene	−2.27 (6)	186	4.08		421
	−63.5	toluene	−1.34 (6)	21.9	34.7		421
[Co(PPIXDME)*N*-MeIm]	−23	toluene	−2.62	417	1.82		404
	−23	DMF	−1.10	12.6	60.3		404
[Co(PPIXDME)*N*-MeIm]	−31	toluene	−2.36 (6)	229	3.32	$\Delta H° = -11.8$ cal mol^{-1}, $\Delta S° = -59$ eu	421, 402
	−37.4	toluene	−2.04 (6)	110	6.93		421, 402
	−45	toluene	−1.70 (6)	50.1	15.2		421, 402
[Co[PPIXDME)2-MeIm][bb]	−10.0	toluene	−2.28 (5)	191	3.99	$\Delta G° = -2.74$ kcal mol^{-1}, $\Delta H° = -14.5$ kcal mol^{-1}, $\Delta S° = -66$ eu	403

TABLE XXXIII. (*Continued*)

complex	T, °C	solvent	log K_{O_2},[at] torr^{-1}	$P_{1/2}$, torr	$P_{1/2}^{-1}$,[c] atm	other constants	ref
[Co(PPIXDME)4-CNPYR]	−45	toluene	−3.8 (3)	6.3×10^3	0.12		421
	−63.5	toluene	−3.3 (3)	2.0×10^3	0.38		421
[Co(PPIXDME)4-*t*-BuPYR]	−37.4	toluene	−3.12 (6)	1.32×10^3	0.577	$\Delta H° = -9.8$ kcal mol^{-1}, $\Delta S° = -56$ eu	421, 402
	−45	toluene	−2.77 (6)	589	1.29		421, 402
	−63.5	toluene	−1.97 (6)	93.3	8.14		421
[Co(PPIXDME)Im]	−31	toluene	−2.50 (6)	316	2.40	$\Delta H° = -11.3$ kcal mol^{-1}, $\Delta S° = -58$ eu	369, 421
	−45	toluene	−1.84 (6)	69.2	11.0		369, 421
	−57.5	toluene	−1.25 (6)	17.8	42.7		369, 421
[Co(PPIXDME)4-NH_2PYR]	−31	toluene	−2.58 (6)	380	2.0	$\Delta H° = -9.9$ kcal mol^{-1}, $\Delta S° = -53$ eu	421
	−37.5	toluene	−2.34 (6)	219	3.47		421
	−45	toluene	−2.05 (6)	112	6.77		421
	−63.5	toluene	−1.20 (6)	15.8	48.0		421
[Co(PPIXDME)PIP]	−31	toluene	−2.92 (6)	832	0.914	$\Delta H° = -9.0$ kcal mol^{-1}, $\Delta S° = -50$ eu	421
	−45	toluene	−2.35 (6)	224	3.39		421
	−63.5	toluene	−1.65 (6)	44.7	17.0		421
[Co(PPIXDME)PYR][bi]	−5.9	toluene	−1.47	29.5	25.8	$\Delta H° = -7.80$ (3) kcal mol^{-1}, $\Delta S° = -48.7$ (1.3) eu	405
	−29.6	toluene	−0.86	7.2	100		405
[Co(PPIXDME)(BzIm)]	−45	toluene	−3.14 (3)[ae]		0.55	$\Delta H° = -9.6$ (6) kcal mol^{-1}, $\Delta S° = -58$ (3) eu	369
	−63.5	toluene	−2.30 (3)[ae]		3.81		369
	−41.6	toluene	−0.41	2.6	2.96×10^2		405
	−52.7	toluene	−0.123	1.33	5.73×10^2		405
[Co(MPIXDME)PYR]	−44.5	toluene	−2.28 (6)	191	3.99	$\Delta G° = 2.38$ kcal mol^{-1}, $\Delta H° = -9.0$ kcal mol^{-1}, $\Delta S° = -50$ eu	403
	−49.5	toluene	−2.15 (6)	141	5.38	$\Delta G° = 2.19$ kcal mol^{-1}	403
	−54.5	toluene	−1.89 (5)	77.6	9.79	$\Delta G° = 1.89$ kcal mol^{-1}	403
	−58.0	toluene	−1.70 (5)	50.1	15.2	$\Delta G° = 1.67$ kcal mol^{-1}	403
[Co(PPIXDME)PYR][bb]	−15.5	DMF	−2.36 (6)	229	3.32	$\Delta G° = 2.77$ kcal mol^{-1}, $\Delta H° = -12.0$ kcal mol^{-1}, $\Delta S° = -57$ eu	403
[Co(MPIXDME)2-MeIm][bb]	−10.0	DMF	−2.15 (4)	141	5.38	$\Delta G° = 2.59$ kcal mol^{-1}, $\Delta H° = -12.9$ kcal mol^{-1}, $\Delta S° = -59$ eu	403
[Co(DPIXDME)PYR]$^{2+}$	−46.0	toluene	−2.49 (1)	309	2.46	$\Delta G° = 2.59$ kcal mol^{-1}, $\Delta H° = -9.9$ kcal mol^{-1}, $\Delta S° = -55$ eu	403
	−49.0	toluene	−2.40 (3)	251	3.03	$\Delta G° = 2.45$ kcal mol^{-1}	403
	−51.0	toluene				$\Delta G° = 2.31$ kcal mol^{-1}	403
	−57.5	toluene				$\Delta G° = 1.99$ kcal mol^{-1}	403
[Co(DPIXDME)PYR][bb]	−15.5	DMF	−2.47 (3)	295	2.58	$\Delta G° = 2.90$ kcal mol^{-1}, $\Delta H° = -13.7$ kcal mol^{-1}	403
[Co(DPIXDME)]$^{2+}$	−10.0	DMF	−2.28 (8)	191	3.99	$\Delta G° = 2.73$ kcal mol^{-1}, $\Delta H° = -13.1$ kcal mol^{-1}, $\Delta S° = -60$ eu	403
[Co(B_{12r})]	−50	DMF	−1.56	36.3	20.9		399
Co-DCC(CH_3)$_2$(CH_2)$_4$	−40.1	CH_3CN	−2.70	500 (5)	1.52		406
Co-DCC(H)$_2$(CH_2)$_5$	−10.1	CH_3CN	−1.7	52 (1)	15		406
Co-DCC(CH_3)$_2$(CH_2)$_5$	−10.1	CH_3CN	−0.600	3.98 (8)	1.91×10^2		406
Co-DCC(H)$_2$(CH_2)$_6$	−10.1	CH_3CN	−0.307	2.03 (3)	3.74×10^2		406
	2.1	CH_3CN	−0.914	8.2 (3)	93		406
Co-DCC(CH_3)$_2$(CH_2)$_6$	−40.1	CH_3CN	3	0.003	3×10^5		406
	−10.1	CH_3CN	0.66	0.22 (5)	3.5×10^3		406
	1.0	CH_3CN	0.12	0.75 (2)	1.0×10^3		406
	20.0	CH_3CN	−0.81	6.5 (2)	1.2×10^2		406
CoTPivPP(*N*-MeIm)	25	toluene	−2.15	140	5.43	$\Delta H° = -12.2$ (3) kcal mol^{-1}, $\Delta S° = 038$ (1) eu[w]	314
	15	toluene	−1.8	70[ak]	12		314
CoTPivPP(1,2-Me_2Im)	25	toluene	−2.95	900	0.844	$\Delta H° = -11.8$ (4) kcal mol^{-1}, $\Delta S° = -40$ (2) eu[w]	314
	15	toluene	−2.43	270[ak]	2.81		314
CoPPIXDME	25	toluene	−4.04	11000	6.9×10^{-2}	$\Delta H° = -9.7$ kcal mol^{-1}, $\Delta S° = -38$ eu[w]	314, 402
CoPPIXDME(*N*-MeIm)	25	toluene	−4.25	17800	4.27×10^{-2}	$\Delta H° = -11.5$ kcal mol^{-1}, $\Delta S° = -45$ eu[w]	145, 314

CoT(p-OCH_3)PP(N-MeIm)	25	toluene	−4.19	15500	4.9×10^{-2}	$\Delta H^\circ = -8.9$ kcal mol^{-1}, $\Delta S^\circ = -36$ eu[w]	145, 314
CoT(p-OCH_3)PP	15	toluene	−4.00	10000[ak]	7.60×10^{-2}		145, 314
CoPPIXDME·DMA	−26.7	toluene				$K = 0.0831\ (38)$ atm^{-1}	407
	−33.9	toluene				$K = 0.1425\ (92)$ atm^{-1}	407
	−43.1	toluene				$K = 0.5126\ (223)$ atm^{-1}, $\Delta H^\circ_{O_2} = -6.6\ (0.7)$ kcal mol^{-1}	407
CoPPIXDME·THTP	−22.8	toluene				$K = 0.0134\ (5)$ atm^{-1}	407
	−34.8	toluene				$K = 0.0300\ (12)$ atm^{-1}, $\Delta H^\circ_{O_2} = -7.6\ (0.6)$ kcal mol^{-1}	407
	−41.1	toluene				$K = 0.0453\ (71)$ atm^{-1}	407
	−45.7	toluene				$K = 0.0645\ (138)$ atm^{-1}	407
CoPPIXDME·PIP	−22.5	toluene				$K = 0.0786\ (82)$ atm^{-1}	407
	−28.8	toluene				$K = 0.1314\ (276)$ atm^{-1}	407
	−40.8	toluene				$K = 0.2927\ (403)$ atm^{-1}	407
CoPPIXDME·HMPA	−15.3	toluene				$K = 0.0273\ (13)$ atm^{-1}	407
	−40.6	toluene				$K = 0.2018\ (55)$ atm^{-1}, $\Delta H^\circ_{O_2} = -8.9\ (0.2)$ kcal mol^{-1}	407
	−51.3	toluene				$K = 0.4335\ (111)$ atm^{-1}	407
CoPPIXDME·PYR	−5.9	toluene				$K = 0.0335\ (10)$ atm^{-1}, $\Delta H^\circ_{O_2} = -8.0\ (0.4)$ kcal mol^{-1}	407
	−29.6	toluene				$K = 0.1377\ (33)$ atm^{-1}	407
	−41.6	toluene				$K = 0.3881\ (144)$ atm^{-1}	407
	−52.6	toluene				$K = 0.7525\ (222)$ atm^{-1}	407
CoPPIXDME·N-MeIm	2	toluene				$K = 0.114\ (6)$ atm^{-1}	407
	−31.0	toluene				$K = 4.27\ (34)$ atm^{-1}, $\Delta H^\circ_{O_2} = -10.0\ (0.2)$ kcal mol^{-1}	407
	−37.4	toluene				$K = 6.37\ (77)$ atm^{-1}	407
	−45.0	toluene				$K = 15.22\ (79)$ atm^{-1}	407

[a] Defined by eq 16 and 20. [b] $K'_{O_2} = [LnCoO_2CoLn]/[Co]^2[L]^{2n}[O_2]$. [c] Values are calculated on the basis of the assumptions outlined in the text. [d] Performed in 15 M NH_3. [e] $K_{O_2} = [(NH_3)_5CoO_2Co(NH_3)_5]a_{H_2O}{}^2/([(Co(NH_3)_5(H_2O))]^2[O_2])$. [f] $K = [Co_2L_2O_2{}^{4+}]/([Co^{2+}]^2[L]^2P_{O_2})$. [g] Determined from oxygen uptake measured polarographically. [h] Determined potentiometrically. [i] Calculated from kinetic data. [j] $K_{O_2}{}^2 = [Co(H_{-1}L)_2O_2Co(H_{-1}L)_2][H^+]^2/([Co(H_{-1}L)(L^-)]^2[O_2])$. [k] $K_{O_2}{}^\circ = [Co(H_{-1}L)_2O_2Co(H_{-1}L)_2]/([Co(H_{-1}L)_2]^2[O_2])$. [l] Too low for accurate determination. [m] $K_{O_2} = [LL'CoO_2CoLL']/([CoLL']^2[O_2])$. [n] Too large for accurate determination. [o] $K_{O_2} = [MH_{-2}LO_2MH_{-2}L^8][H^+]^4/[ML^{2-}]^2P_{O_2}$. [p] $K = [ML_2(OH)(O_2)ML_2]/([ML_2OHML_2][O_2])$. [q] K_{O_2} defined by eq 13. [r] $K'_{O_2} = [CoLO_2(OH)CoL][H^+]/([Co^{2+}]^2[L]^2[O^2])$. [s] $K_{O_2} = [CoL_2(O_2)(OH)CoL_2][H^+]/([Co^{2+}]^2[L]^4P_{O_2})$. [t] $K_{O_2} = [CoLO_2(OH)CoL][H^+]/([Co^{2+}]^2[L]^2P_{O_2})$. [u] These constants omitted since hydroxo bridging was neglected. [v] $K_{ML} = [Co(TRIEN)^{2+}]/[Co^{2+}][TRIEN]$. [w] Standard state is 1 atm of O_2. [x] $K_{OH} = [CoL_2O_2(OH)CoL_2][H^+]/[CoL_2O_2CoL_2]$. [y] Could not measure equilibria due to rapid irreversible oxidation to Co(III) complexes. [z] $K_{OH} = [ML_2OHML_2][H^+]/[ML_2]^2$. [aa] Calculated from constant given, assuming $K_W = 10^{-13.795}$. [ab] $K_{(CoL)_2O_2(OH)} = [CoL]^2[O_2][OH^-]/[(CoL)_2O_2(OH)]$. [ac] $K_{O_2} = [Co_2(H_{-1}L)_2(O_2)(OH)][H^+]^3/[ML]^2[O_2]$. [ad] $K'_{O_2} = [Co_2(H_{-1}L)_2O_2(OH)][H^+]/([Co(H_{-1}L)]^2[O_2])$. [ae] $K_{O_2} = [LCoP(O_2)]/([LCoP][P_{O_2}])$. [af] $K_{O_2} = [Ni(H_{-2}L)O_2]/[Ni(H_{-2}L)][O_2]$. [ag] $K_{O_2} = [(FeL)_2O_2]/([FeL]^2[O_2])$. [ah] $K'_{O_2} = [(FeL)_2O_2]/([Fe^{2+}]^2[L]^2[O_2])$. [ai] Defined by eq 17. [aj] Values are determined from the provided graphs of percent oxygenation vs. O_2 pressure. [ak] Interpolated from ΔH° and ΔS° values. [al] Defined by eq 5. [am] Defined by eq 20. [an] No dioxygen complex formation. [ao] K_{O_2} is reported as M^{-1}. [ap] pH 7.3, Na_2PO_4 buffer, 2% cetyltrimethylammonium bromide. [aq] Activation parameters for the addition of O_2 to the complexes. [ar] Activation parameters for the dissociation of O_2 from the Vaska-type complex. [as] Net ΔH°_2 and ΔS°_2 values for the reversible reaction. [at] $K_{O_2} = [CoL{\cdot}O_2]/[CoL]P_{O_2}$ or $K_{O_2} = [CoL{\cdot}B{\cdot}O_2]/[CoL{\cdot}B]P_{O_2}$. [au] Standard state of 1.00 torr for O_2 except as otherwise noted. [av] $K_T = [CoL(B)(O_2)]/[CoL][B][O_2]$. [aw] Standard state $[O_2] = 1$ mol dm^{-3}. [ax] Calculated by combining constants obtained in pyridine and chloroform solvents. [ay] Value of K_Y extrapolated from higher temperature. [az] Assuming solubility of oxygen in PYR is 8.6×10^{-4} M at 20 °C and 156 torr. [ba] In 1.8% base/solvent solution. [bb] Data at other temperatures are omitted here. [bc] Calculated from activation parameters. [bd] Reported as K_{O_2}. [be] $K_{O_2} = [CoP(B)(O_2)]/[CoP(B)][O_2]$. Standard state $[O_2] = 1$ M. [bf] $K_4 = [CoP(B)(O_2)]/[CoP(B)_2][O_2]$. [bg] Estimated standard deviation is 1–2 kcal mol^{-1}. [bh] Estimated standard deviation is 3–4 eu. [bi] High O_2 pressures used to obtain more accurate constants. [bj] 10% N-methylpyrrolidone–90% toluene.

TABLE XXXIV. Equilibrium Constants for Reaction of Natural Oxygen Carriers with O_2

protein	T, °C	pH	other conditions	$P_{1/2}$, torr	$P_{1/2}^{-1}$, atm^{-1}	n^a	other constants	ref
			A. Hemoglobins					
human HbA	25	7.4	0.05 M BIS-TRIS buffer, 1.5×10^{-5} M Hb	1.9	4.0×10^2	2.51		434
	25	9.1	0.05 M glycine-NaOH buffer, 1.5×10^{-5} M Hb	1.2	6.3×10^2	2.11		434
	20	7.0	0.01 M TRIS-HCl buffer	1.81	4.20×10^2	2.4		435
	10	7.07	0.1 M potassium phosphate buffer	3.42	2.22×10^2	2.75		436
	20-21	7.4	0.1 M potassium phosphate buffer	4.5	1.7×10^2			433
	25	7.4	0.05 M BIS-TRIS-HCl buffer, 1.5×10^5 M Hb	1.9	4.0×10^2	2.51	$P_m = 2.56^b$	437
	25	7.4	0.05 M BIS-TRIS buffer, 1.5×10^{-5} M Hb	2.38[c]	3.19×10^2	2.78[c]		438
	25	7.4	0.05 M BIS-TRIS buffer, 0.1 M NaCl, 1.5×10^{-5} M Hb	4.35	1.75×10^2	2.87		438
	25	7.4	0.05 M BIS-TRIS buffer, 1.5×10^{-5} M Hb	1.9	4.0×10^2	2.51	$K_T = 0.115$ (6) torr^{-1}, $K_r = 4.31$ (15) torr^{-1}	434
		8.8		1.2	6.3×10^2	2.73		440
		7.4		4.7	1.6×10^2	3.05		440
		7.0		7.7	99	2.86		440
		6.5		12.5	61	3.00		440
	25	7.4	0.05 M BIS-TRIS, 0.1 M NaCl	4.60	1.65×10^2			440
	30	7.4	0.05 M BIS-TRIS, 0.1 M NaCl	6.68	1.14×10^2			440
	35	7.4	0.05 M BIS-TRIS, 0.1 M NaCl	9.17	82.9			440
	37	7.4	0.05 M BIS-TRIS, 0.15 M NaCl	26	29	2.68		441
	10	7.4	0.05 M BIS-TRIS, 1.5×10^{-5} M Hb	1.64	4.63×10^2	3.02		442
	15	7.4	0.05 M BIS-TRIS, 1.5×10^{-5} M Hb	2.30	3.30×10^2	2.84		442
	20	7.4	0.05 M BIS-TRIS, 1.5×10^{-5} M Hb	3.49	2.18×10^2	2.81		442
	25	7.4	0.5 M BIS-TRIS, 1.5×10^{-5} M Hb	4.32	1.76×10^2	2.76		442
	30	7.4	0.5 M BIS-TRIS, 1.5×10^{-5} M Hb	6.73	1.13×10^2	2.81		442
	25	7.0					$\Delta H^\circ = -13.4$ kcal mol^{-1}	343
	15	7.4	0.05 M BIS-TRIS, 0.1 M Cl$^-$				$K_T = 0.020$ torr^{-1} [d], $K_R = 38$ torr^{-1} [d]	445
	25	7.4	0.05 M BIS-TRIS, 1.25×10^{-5} M Hb	1.9	4.0×10^2	2.52		512
	25	7.4	0.05 M BIS-TRIS, 1.25×10^{-5} M Hb, 0.1 M NaCl, 0.1 M phosphate	5.6	1.4×10^2	2.95		512
	25			7.1	1.1×10^2			447
	20	6.71	0.05 M BIS-TRIS buffer, 0.05 mM Hb, 0.1 M Cl$^-$				$\log P_{1/2} = 0.85$	470
	20	7.02	0.05 M BIS-TRIS buffer, 0.05 mM Hb, 0.1 M Cl$^-$				$\log P_{1/2} = 0.70$	470
	20	7.29	0.05 M BIS-TRIS buffer, 0.05 mM Hb, 0.1 M Cl$^-$				$\log P_{1/2} = 0.53$	470
	20	6.71	0.05 M BIS-TRIS, 0.05 mM Hb, 0.1 M Cl$^-$, 0.20 mM Zn^{2+}				$\log P_{1/2} = 0.30$	470
	20	7.02	0.05 M BIS-TRIS, 0.05 mM Hb, 0.1 M Cl$^-$, 0.20 mM Zn^{2+}				$\log P_{1/2} = 0.06$	470
	20	7.29	0.05 M BIS-TRIS, 0.05 mM Hb, 0.1 M Cl$^-$, 0.20 mM Zn^{2+}				$\log P_{1/2} = -0.11$	470
	20	7.0	0.05 M BIS-TRIS buffer	2.8			$\log P_{1/2} = 0.41$	472

20	7.3	0.05 M BIS-TRIS buffer	2.65			$\log P_{1/2} = 0.09$	472
20	7.6	0.05 M BIS-TRIS buffer			2.65	$\log P_{1/2} = -0.08$	472
20	7.0	0.05 M BIS-TRIS buffer, 1×10^{-3} M DPG			2.7	$\log P_{1/2} = 1.12$	472
20	7.3	0.05 M BIS-TRIS buffer, 1×10^{-3} M DPG			2.7	$\log P_{1/2} = 0.96$	472
20	7.6	0.05 M BIS-TRIS buffer, 1×10^{-3} M DPG			2.65	$\log P_{1/2} = 0.81$	472
20	7.68	0.05 M TRIS-HCl, 10 mM $CaCl_2$, = 0.13	24	32	2.02		490
20	8.56	0.05 M TRIS-HCl, 10 mM $CaCl_2$, = 0.13	5	2×10^2	1.98		490
20	9.55	0.05 M ethanolamine, 10 mM $CaCl_2$, = 0.13	3.7	2.1×10^2	1.90		490
20	9.68	0.05 M ethanolamine, 10 mM $CaCl_2$, = 0.13	4	2×10^2	1.70		490
20	7.6	0.05 M TRIS-HCl, 10 mM $CaCl_2$, = 0.1	10	76	1.4		490
20	7.6	0.05 M TRIS-HCl, 10 mM Ca^{2+}, = 0.13	24	32	2.02		490
20	7.6	0.05 M TRIS-HCl, 25 mM Ca^{2+}, = 0.17	26	29	2.35		490
20	7.6	0.05 M TRIS-HCl, 50 mM Ca^{2+}, = 0.25	23	33	2.45		490
20	7.6	0.05 M TRIS-HCl, 75 mM Ca^{2+}, = 0.32	22.8	33.3	2.45		490
20	7.6	0.05 M TRIS-HCl, 100 mM Ca^{2+}, = 0.40	22.5	33.8	2.68		490
20	9.1	0.0015–0.002 M Hb	0.55	1.4×10^3	2.0		491
20	9.1	0.0015–0.002 M Hb, 0.001 M IHP	0.95	8.0×10^2	1.0–2.36		491
20	7.3	0.05 M BIS-TRIS, 5×10^{-5} M Hb	0.52	1.5×10^3	2.4		499
20	7.3	0.05 M BIS-TRIS, 5×10^{-5} M Hb, 2.5×10^{-4} M DPG	0.95	8.0×10^2	2.8		
20	7.3	stripped, spectrin in amounts equimolar with Hb, 1.2×10^{-4}, 2,3-DPG	4.7	1.6×10^2			465
25	7.4	stripped, 0.02 M BIS-TRIS buffer, 8×10^{-5} M Hb	1.71	4.44×10^2			467
25	7.4	stripped, 0.02 M BIS-TRIS buffer, 8×10^{-5} M Hb, 5×10^{-5} M DPG	6.67	1.14×10^2			467
25	7.4	stripped, 0.02 M BIS-TRIS buffer, 8×10^{-5} M Hb, 1×10^{-3} M DPG	6.67	1.14×10^2			467
25	7.4	stripped, 0.02 M BIS-TRIS buffer, 8×10^{-5} M Hb, 4.5×10^{-5} M Zn^{2+}	0.46	1.7×10^3			467
25	7.4	stripped, 0.02 M BIS-TRIS buffer, 8×10^{-5} M Hb, 4.5×10^{-5} M Zn^{2+}, 5×10^{-5} M DPG	1.88	4.04×10^2			467
25	7.4	stripped, 0.02 M BIS-TRIS buffer, 8×10^{-5} M Hb, 4.5×10^{-5} M Zn^{2+}, 1×10^{-3} M DPG	3.62	2.10×10^2			467
	~9	stripped, 0.1 M TRIS-HCl				$\Delta H = -14.6$ kcal/mol	488

TABLE XXXIV (*Continued*)

					log $[L(C_A)/L(O)]^f$				
				C_A[e]	methanol	ethanol	L-propanol	*n*-proponol	
	21.8	7.0	0.1 M phosphate	2.5	0.31	0.46	0.52	0.67	492
				5	0.62	0.78	0.89	1.10	492
				7	0.74	1.06	1.17	1.34	492
				10	0.97	1.49	1.56	1.56	492
				12.5	1.10	1.66	1.78	1.65	492
				15	1.23	1.82	2.03	1.69	492

protein	T, °C	pH	other conditions	$P_{1/2}$, torr	$P_{1/2}^{-1}$, atm^{-1}	n^a	other constants	ref
human HbA + DPG	25	7.4	2 mM DPG, 0.05 M BIS-TRIS, 1.25×10^{-5} M Hb	15.3	49.7	3.02		512
	25	7.4	2 mM DPG, 0.05 M BIS-TRIS, 1.25×10^{-5} M Hb, 0.1 M NaCl	15.1	50.3	2.93		512
	25	7.4	2 mM DPG, 0.05 M BIS-TRIS, 1.25×10^{-5} M Hb, 0.1 M NaCl	15.5	49.0	3.05	$P_m = 14.56$[b]	437
human HbA + DPG[g]	25	7.4	2 mM DPG, 0.05 M BIS-TRIS, 1.5×10^{-5} M Hb	15.3	49.7	3.09		434
	25	9.1	2 mM DPG, 0.05 M glycine-NaOH, 1.5×10^{-5} M Hb	1.6	4.8×10^2	2.38		434
	25	7.4	2 mM DPG, 0.05 M BIS-TRIS, 0.1 M NaCl	11.6	65.6			443
	30	7.4	2 mM DPG, 0.05 M BIS-TRIS, 0.1 M NaCl	15.3	49.7			443
	35	7.4	2 mM DPG, 0.05 M BIS-TRIS, 0.1 M NaCl	20.2	37.6			443
	20	7.0	0.3 mM DPG, 0.01 M TRIS-HCl	10.7	71.0	2.8		435
	25	7.4	2 mM DPG, 0.05 M BIS-TRIS, 1.5×10^{-5} M Hb	15.3	49.7	3.09	$P_m = 14.6$[b]	437
	25	7.4	2 mM DPG, 0.05 M BIS-TRIS	12.1	62.8	3.07		438
	25	7.4	2 mM DPG, 0.05 M BIS-TRIS, 0.1 M NaCl	13.2	57.6	3.11		438
human HbA + IHP[g]	25	7.4	2 mM IHP, 0.05 M BIS-TRIS, 0.1 M NaCl	40.9	18.6			443
	30	7.4	2 mM IHP, 0.05 M BIS-TRIS, 0.1 M NaCl	54.1	14.0			443
	35	7.4	2 mM IHP, 0.05 M BIS-TRIS, 0.1 M NaCl	72.2	10.5			443
	25	7.4	1.7 mM IHP, 0.05 M BIS-TRIS, 1.5×10^{-5} M Hb	70.8	10.7	2.83	$P_m = 65.1$[b]	437
	25	7.4	2 mM IHP, 0.05 M BIS-TRIS	50.3	15.1	2.41		438
	25	7.4	2 mM IHP, 0.05 M BIS-TRIS, 0.1 M NaCl	44.0	17.3	2.62		438
human HbA 1st O_2	25[h]	7.4					$\Delta H° = -13.4$ kcal mol^{-1} $K = 0.32$ torr^{-1},[i] $\Delta H° = -25.1$ (2.8) kcal mol^{-1} $\Delta G° = -3.25$ kcal mol^{-1},[j] $\Delta S° = -73$ (9) cal deg^{-1} mol^{-1} [j]	444
human HbA 2nd O_2	25[h]	7.4					$K = 0.44$ torr^{-1},[j] $\Delta H° = -12.6$ (3.0) kcal mol^{-1} $\Delta G° = -3.45$ kcal mol^{-1},[j] $\Delta S° = -31$ (10) cal deg^{-1} mol^{-1} [j]	444
human HbA 3rd O_2	25[h]	7.4					$K = 0.50$ torr^{-1},[i] $\Delta H° = -12.5$ (3.0) kcal mol^{-1}	444

							$\Delta G^\circ = -3.45$ kcal mol^{-1},[j] $\Delta S^\circ = -31$ (10) cal deg^{-1} mol^{-1}[j]	
human HbA 3rd O_2	25[h]	7.4					$K = 0.50$ torr^{-1},[i] $\Delta H^\circ = -12.5$ (3.0) kcal mol^{-1}	444
							$\Delta G^\circ = -3.52$ kcal mol^{-1},[j] $\Delta S^\circ = -30$ (10) cal deg^{-1} mol^{-1}[j]	
human HbA 4th O_2	25[h]	7.4					$K = 1.09$ torr^{-1},[i] $\Delta H^\circ = -10.1$ (1.4) kcal mol^{-1}	444
							$\Delta G^\circ = -3.98$ kcal mol^{-1},[j] $\Delta S^\circ = -25$ (5) cal deg^{-1} mol^{-1}[j]	
human Hb α chain	25	7.40	0.1 M TRIS, 0.1 M Cl^-, 1 mM Na_2EDTA	0.74	1.0×10^3		$\Delta H^\circ = -14.2$ (6) kcal/mol, $\Delta S^\circ = -2.05$ (22) $\times 10^{-2}$ kcal/mol K	482
	25	7.3	0.2 M sodium phosphate	0.53	1.4×10^3			447
	25	7.4	0.1 M phosphate buffer	0.63	1.2×10^2	1.0		512
	24[k]	7.4	0.1 M phosphate buffer	0.58	1.3×10^3		$\Delta H^\circ = -15.9$ kcal mol^{-1}[l]	513
human Hb β chain	25	7.4	0.1 M phosphate buffer	0.24	3.2×10^3	1.0		512
	24[k]	7.4	0.1 M phosphate buffer	0.29	2.6×10^3		$\Delta H^\circ = -18.5$ kcal mol^{-1}[l]	513
	25	7.3	0.2 M sodium phosphate	0.30	2.5×10^3			447
	25	7.40		0.42	1.8×10^3		$\Delta H^\circ = -16.9$ (8) kcal/mol, $\Delta S^\circ = -2.86$ (28) $\times 10^{-2}$ kcal/mol K	482
human HbF[m]	25	7.4	0.05 M BIS-TRIS, 1.5×10^{-5} M Hb	2.7	2.8×10^2	2.44	$P_m = 2.56$[b]	437
	25	7.4	2 mM DPG, 0.05 M BIS-TRIS, 1.5×10^{-5} M Hb	8.9	85	2.98	$P_m = 8.21$[b]	437
human Hb Barcelona	37	7.4	0.05 M BIS-TRIS, 0.15 M NaCl	21	36	2.4		441
human Hb Bethesda	25	7.4	0.05 M BIS-TRIS	0.32	2.4×10^3			438
	25	7.4	2 mM DPG, 0.05 M BIS-TRIS	0.61	1.2×10^3			438
	25	7.4	2 mM IHP, 0.05 M BIS-TRIS	2.21	3.44×10^2			438
human Hb Capetown	10	7.16	0.1 M potassium phosphate buffer	1.33	5.71×10^2	2.23		436
human Hb Chesapeake	10	7.04	0.1 M potassium phosphate buffer	0.43	1.8×10^3	1.37		436
	25	7.4	0.05 M BIS-TRIS	0.39	1.9×10^3	1.22		438
	25	7.4	0.05 M BIS-TRIS, 0.1 M NaCl	0.79	9.6×10^2	1.52		438
	25	7.4	2 mM DPG, 0.06 M BIS-TRIS	1.83	4.15×10^2	1.83		438
	25	7.4	2 mM DPG, 0.05 M BIS-TRIS, 0.1 M NaCl	1.96	3.88×10^2	2.00		438
	25	7.4	2 mM IHP, 0.05 M BIS-TRIS	7.82	97.2	2.15		438
	25	7.4	2 mM IHP, 0.05 M BIS-TRIS, 0.1 M NaCl	7.12	10.7	2.28		438
human Hb Hiroshima	20	7.0	0.01 M TRIS-HCl	0.31	2.5×10^3	1.1		435
	20	7.0	0.3 mM DPG, 0.01 M TRIS-HCl	1.84	4.13×10^2	1.9		435
human Hb Ranier	25	7.4	0.05 M BIS-TRIS	0.18	4.2×10^3			438
	25	7.4	0.05 M BIS-TRIS, 2 mM DPG	0.64	1.2×10^3			438
	25	7.4	0.05 M BIS-TRIS, 1.5 mM IHP	1.24	6.13×10^2			438
Hb G β Ferrara	20	7.0	0.05 M BIS-TRIS buffer			2.8	$\log P_{1/2} = 0.42$	472
	20	7.3	0.05 M BIS-TRIS buffer			2.65	$\log P_{1/2} = 0.2$	472
	20	7.6	0.05 M BIS-TRIS buffer			2.65	$\log P_{1/2} = 0.12$	472
	20	7.0	0.05 M BIS-TRIS buffer, 1×10^{-3} M DPG			2.6	$\log P_{1/2} = 0.96$	472
	20	7.3	0.05 M BIS-TRIS buffer, 1×10^{-3} M DPG			2.6	$\log P_{1/2} = 0.78$	472
	20	7.6	0.05 M BIS-TRIS buffer, 1×10^{-3} M DPG			2.7	$\log P_{1/2} = 0.63$	472

TABLE XXXIV (*Continued*)

protein	T, °C	pH	other conditions	$P_{1/2}$, torr	$P_{1/2}^{-1}$, atm^{-1}	n^a	other constants	ref
Hb Hirose (SER for TRP at C-3(37)β)	37	7.3	0.05 M BIS-TRIS, 0.1 M Cl^{-1}, 1 mM EDTA, 60 μM heme, 105 μM 2,3-DPG	5.1	1.5×10^2	1.3		478
human Hb (CPA)	25	7.4	0.05 M BIS-TRIS	0.13	5.8×10^3			438
	25	7.4	2 mM DPG, 0.05 M BIS-TRIS	0.22	3.5×10^3			438
	25	7.4	2 mM IHP, 0.05 M BIS-TRIS	1.88	4.04×10^2			438
	25	7.4	0.05 M BIS-TRIS, 1.5×10^{-5} M Hb	0.44	1.7×10^3	1.5	K_T = 1.87 (44) $torr^{-1}$,[d] K_R = 5.54 (1.07) $torr^{-1}$ [d]	439
	25	7.4	2 mM DPG, 0.05 M BIS-TRIS, 1.5×10^{-5} M Hb	0.44	1.7×10^3	1.23	K_T = 1.80 (80) $torr^{-1}$,[d] K_R = 7.05 (2.42) $torr^{-1}$ [d]	439
human Hb (IAA)	25	7.4	0.05 M BIS-TRIS	1.19	6.39×10^2			438
	25	7.4	2 mM DPG, 0.05 M BIS-TRIS	7.82	97.2			438
	25	7.4	2 mM IHP, 0.05 M BIS-TRIS	24.5	31.0			438
	25	7.4	0.05 M BIS-TRIS, 1.5×10^{-5} M Hb	1.2	6.3×10^2	1.63	K_T = 0.406 (106) $torr^{-1}$,[d] K_R = 7.78 (1.55) $torr^{-1}$ [d]	439
	25	7.4	2 mM DPG, 0.05 M BIS-TRIS, 1.5×10^{-5} M Hb	8.5	89	2.71	K_T = 0.0253 (41) $torr^{-1}$,[d] K_R = 3.17 (39) $torr^{-1}$ [d]	439
human Hb (NEM)	25	7.4	0.05 M BIS-TRIS	1.24	6.13×10^2			438
	25	7.4	2 mM DPG, 0.05 M BIS-TRIS	4.57	1.66×10^2			438
	25	7.4	2 mM IHP, 0.05 M BIS-TRIS	18.6	40.9			438
	25	7.4	0.05 M BIS-TRIS, 1.5×10^{-5} M Hb	1.2	6.3×10^2	1.44	K_T = 0.355 (11) $torr^{-1}$, K_R = 1.82 (5) $torr^{-1}$	439
	25	7.4	2 mM DPG, 0.05 M BIS-TRIS, 1.5×10^{-5} M Hb	4.7	1.6×10^2	2.27	K_T = 0.0398 (30) $torr^{-1}$, K_R = 1.30 (7) $torr^{-1}$	439
HbA-4-ITCB	20	7.3	0.5 M BIS-TRIS, 5×10^{-5} M Hb	0.91	8.4×10^2	1.8		499
	20	7.3	0.5 M BIS-TRIS, 5×10^{-5} M Hb, 2.5×10^{-4} M DPG	1.15	6.61×10^2	2.1		499
HbA-4-ICSA	20	7.3	0.5 M BIS-TRIS, 5×10^{-5} M Hb	0.4	2×10^3	2.1		499
	20	7.3	0.5 M BIS-TRIS, 5×10^{-5} M Hb, 2.5×10^{-4} M DPG	0.62	1.2×10^3	2.4		499
mesopor α chain	23	7.0	0.1 M phosphate buffer	1.4	5.4×10^2	1.7		476
mesopor β chain	23	7.0	0.1 M phosphate buffer	1.4	5.4×10^2	1.7		476
protopor α chain	23	7.0	0.1 M phosphate buffer	13	58	2.5		476
protopor β chain	23	7.0	0.1 M phosphate buffer	13	58	2.5		476
α(meso)β(proton)	23	7.0	0.1 M phosphate buffer	3.7	$\sim 1 \times 10^2$	1.7		476
α(proton)β(meso)	23	7.0	0.1 M phosphate buffer	3.3	2.3×10^2	1.7		476
proto Hb	20	7.0	0.1 M phosphate buffer	10	76	2.8		475
protoheme Hb^o	22-23	7.0	0.1 M potassium phosphate buffer	125.0	6.08	2.2	ΔH° = −7.5 (5) kcal mol^{-1},[p] ΔS° = −21.9 (8) $eu^{p,q}$	446
mesoheme Hb^o	22-23	7.0	0.1 M potassium phosphate buffer	40.0	19.0	1.2	ΔH° = −8.0 (5) kcal mol^{-1},[p] ΔS° = −21.5 (8) $eu^{p,q}$	446
deuteroheme Hb^o	22-23	7.0	0.1 M potassium phosphate buffer	60.0	12.7	1.5	ΔH° = −10.7 (5) kcal mol^{-1},[p] ΔS° = −31.4 (8) $eu^{p,q}$	446
$\alpha_2^+(CN)\beta_2(O_2)Hb^r$	25	7.4	0.05 M BIS-TRIS, 1.25×10^{-5} M Hb	0.30	2.5×10^3	1.08		512
	25	7.4	0.05 M BIS-TRIS, 1.25×10^{-5} M Hb, 0.1 M NaCl	0.40	1.9×10^3	1.17		512
	25	7.4	2 mM DPG, 0.05 M BIS-TRIS, 1.25×10^{-5} M Hb	1.41	5.39×10^2	1.41		512
	25	7.4	2 mM DPG, 0.05 M BIS-TRIS, 1.25×10^{-5} M Hb, 0.1 M NaCl	1.38	5.51×10^2	1.52		512
$\alpha_2(O_2)\beta_2^+(CN)Hb$	25	7.4	0.04 M BIS-TRIS, 1.25×10^{-5} M Hb	0.40	1.9×10^3	1.15		512

	25	7.4	0.05 M BIS-TRIS, 1.25×10^{-5} M Hb, 0.1 M NaCl	0.47	1.6×10^3	1.10		512
	25	7.4	2 mM DPG, 0.05 M BIS-TRIS, 1.25×10^{-5} M Hb	0.83	9.2×10^2	1.13		512
	25	7.4	2 mM DPG, 0.05 M BIS-TRIS, 1.25×10^{-5} M Hb, 0.1 M NaCl	0.79	9.6×10^2	1.14		512
des(Arg-141)α	25	7.3	0.2 M sodium phosphate	0.47	1.6×10^3			447
des(Arg-141, Tyr-140)α	25	7.3	0.2 M sodium phosphate	0.38	2.0×10^3			447
des(Arg-141, Tyr-140, Lys-139)α	25	7.3	0.2 M sodium phosphate	0.29	2.6×10^3			447
des(His-146)β	25	7.3	0.2 M sodium phosphate	0.60	1.3×10^3			447
des β^s	25	7.3	0.2 M sodium phosphate	0.95	8.0×10^3			447
$\beta^{PMB\ s}$	25			2.65	2.87×10^2			448
Sulf Hb	0	8.25		63.4	12.0	1.0		479
2-formyl-4-vinyl-(spirographis) Hb	20	7.0	0.1 M phosphate buffer	6	1×10^2	1.7		475
2-vinyl-4-formyl-(isospirographis) Hb	20	7.0	0.1 M phosphate buffer	2.1	3.6×10^2	1.1		475
2,4-diformul Hb	20	7.0	0.1 M phosphate buffer	4.3	1.8×10^2	1.0		475
CoHb	14–15	7.0	0.2 M phosphate buffer, 0.3 M NaCl	20.5	37.1	2.3		462
	15	7.0	0.05 M BIS-TRIS	17	45			445
	15	7.4	0.05 M BIS-TRIS, 0.1 M NaCl	40	19		$K_R = 0.0036$ torr^{-1}, $K_R = 0.075$ torr^{-1}	445
	15	7.4	2 mM DPG, 0.05 M BIS-TRIS	80	9.5			445
	15	7.4	2 mM DPG, 0.05 M BIS-TRIS, 0.1 M NaCl	92	8.3			445
	15	7.4	2 mM IHP, 0.05 M BIS-TRIS	320	2.38			445
	15	7.4	2 mM IHP, 0.05 M BIS-TRIS, 0.1 M NaCl	290	2.62			445
	15	7.4	0.1 M phosphate	68	11			445
CoHb$\alpha^{-PMB\ t}$	15	7.4	0.1 M phosphate buffer	26.9	28.3			513
	24	7.4	0.1 M phosphate buffer	64.2	11.8		$\Delta H^\circ = -14.8$ kcal mol^{-1}, $\Delta S^\circ = -58.1$ eu[u]	513
CoHb$\alpha^{-SH\ t}$	15	7.4	0.1 M phosphate buffer	24.3	31.3			513
	24	7.4	0.1 M phosphate buffer	52.5	14.5		$\Delta H^\circ = -14.6$ kcal mol^{-1}, $\Delta S^\circ = -60.0$ eu[v]	513
CoHbβ^{-PMB}	15	7.4	0.1 M phosphate buffer	106.9	7.109			513
	24	7.4	0.1 M phosphate buffer	238.6	3.185		$\Delta H^\circ = -13.9$ kcal mol^{-1}, $\Delta S^\circ = -54.5$ eu[v]	513
CoHbβ^{-SH}	15	7.4	0.1 M phosphate buffer	24.5	31.0			513
	24	7.4	0.1 M phosphate buffer	60.2	12.6		$\Delta H^\circ = -16.5$ kcal mol^{-1}, $\Delta S^\circ = -63.8$ eu[v]	513
horse Hb	20			0.43	1.8×10^3			460
	4	7.3	0.05 M BIS-TRIS	1.62	4.69×10^2			449
	4	9.4	0.05 M BIS-TRIS	0.34	2.2×10^3			449
	4	7.3	0.2 mM DPG, 0.05 M BIS-TRIS	109.6	6.93			449
	4	9.4	0.2 mM DPG, 0.05 M TRIS	0.34	2.2×10^3			449
horse proto Hb	20	7.0	0.10 M phosphate buffer	10.0	76.0	2.6		471
horse deutero Hb	20	7.0	0.05 M BIS-TRIS buffer	1.2	6.3×10^2	2.4		471
	20	7.0	0.10 M phosphate buffer	4.6	1.7×10^2	2.1		471
horse meso Hb	20	7.0	0.05 M BIS-TRIS buffer	0.6	1×10^3	1.8		471
	20	7.0	0.10 M phosphate buffer	1.0	7.6×10^2	1.3		471
native horse Hb	20	7.0	0.05 M BIS-TRIS buffer	2.6	3.3×10^2	2.7		471
	20	7.0	0.10 M phosphate buffer	11.4	66.7	2.8		471

TABLE XXXIV (*Continued*)

protein	T, °C	pH	other conditions	$P_{1/2}$, torr	$P_{1/2}^{-1}$, atm^{-1}	n^a	other constants	ref
Glycera dibranchiata protoheme Hb^w	5	7.4	0.1 M phosphate buffer	1.6	4.7×10^2			450
Chironomus thumni thumni HbIII	15	5–10	0.2 M phosphate, 0.2 M TRIS-HCl, or 0.2 M borate–carbonate				$P_{1/2max} = 0.72$, $P_{1/2max} = 0.29$, $\Delta G°_{max} = -7.76$ kcal mol^{-1}, $\Delta G°_{min} = -8.28$ kcal mol^{-1}	451
	25	5–10	0.2 M phosphate, 0.2 M TRIS-HCl, or 0.2 M borate–carbonate				$P_{1/2max} = 1.60$, $P_{1/2min} = 0.68$, $\Delta G°_{max} = -7.64$ kcal mol^{-1}, $\Delta G°_{min} = -8.15$ kcal mol^{-1}	451
	37	5–10	0.2 M phosphate, 0.2 M TRIS-HCl, or 0.2 M borate–carbonate				$P_{1/2max} = 4.00$, $P_{1/2min} = 1.79$, $\Delta G°_{max} = -7.50$ kcal mol^{-1}, $\Delta G°_{min} = -7.99$ kcal mol^{-1}	451
		5–10	0.2 M phosphate, 0.2 M TRIS-HCl, or 0.2 M borate–carbonate				$\Delta H°_{max} = -11.7$ kcal mol^{-1}, $\Delta H°_{min} = -12.08$ kcal mol^{-1}, $\Delta S°_{max} = -11.8$ cal deg^{-1} mol^{-1}, $\Delta S°_{min} = -13.2$ cal deg^{-1} mol^{-1}	451
Chironomus thumni thumni HbIV	15	5-10	0.2 M phosphate, 0.2 M TRIS-HCl, or 0.2 M borate–carbonate				$P_{1/2max} = 1.51$, $P_{1/2min} = 0.21$, $\Delta G°_{max} = -7.34$ kcal mol^{-1}, $\Delta G°_{min} = -8.47$ kcal mol^{-1}	451
	25	5–10	0.2 M phosphate, 0.2 M TRIS-HCl, or 0.2 M borate–carbonate				$P_{1/2max} = 2.75$, $P_{1/2min} = 0.45$, $\Delta G°_{max} = -7.32$ kcal mol^{-1}, $\Delta G°_{min} = -8.40$ kcal mol^{-1}	451
	37	5–10	0.2 M phosphate, 0.2 M TRIS-HCl, or 0.2 M borate–carbonate				$P_{1/2max} = 5.35$, $P_{1/2min} = 1.09$, $\Delta G° = -7.32$ kcal mol^{-1}, $\Delta G°_{min} = -8.30$ kcal mol^{-1} $\Delta H°_{max} = -7.60$ kcal mol^{-1}, $\Delta H°_{min} = -10.70$ kcal mol^{-1} $\Delta S°_{max} = -0.91$ cal deg^{-1} mol^{-1}, $\Delta S°_{min} = -7.7$ cal deg^{-1} mol^{-1}	451
Chironomus Hb protoheme^w	20	7	0.2 M phosphate	0.7	1.1×10^3			452
Chironomus Hb mesoheme^w	20	7	0.2 M phosphate	0.27	2.8×10^3			452
Chironomus Hb deuteroheme^w	20	7	0.2 M phosphate	0.13	5.8×10^3			452
Gastrophilus Hb	39		1×10^{-3} g mol hematin/L	4.9	1.6×10^2			453
	39		8.4×10^{-5} g mol hematin/L	>0.02	$<4 \times 10^4$			453
	25	7.0	0.2 M sodium phosphate buffer	0.02			$K_{O_2} = 1 \times 10^7$ M^{-1} [x]	454
				0.02	4×10^4			448
Ascaris body wall fluid Hb	20	6.2–8.9		0.11	6.9×10^3			455, 511
	37	6.2–8.9		0.5	2×10^3			455
Ascaris perienteric fluid Hb	20	6.2–8.9		0.0015	5.1×10^5			455
	37	6.2–8.9		0.01	8×10^4			455
earthworm Hb	20-21	7.4	0.1 M potassium phosphate buffer	8.2	93	4		511

tubifex Hb	20–21	7.4	0.1 M potassium phosphate buffer	0.9	8×10^2	1.3		511
Candida mycoderma (yeast) Hb		7.0	0.1 M phosphate buffer, 3% NaCl, 10 mM glucose, catalase[y]	0.01	8×10^4		$P_{1/2} = 2 \times 10^{-8}$ M	456
Paramecium Hb				0.6	1×10^3		$P_{1/2} = 9.3 \times 10^{-7}$ M	456, 457
Glycera dibranchiata Co protoporphyrin Hb[w]	4	7.4	0.1 M phosphate buffer	700	1.09			450
sea cucumber *Thyonella gemmata*	20	7	0.05 M potassium phosphate				$\bar{x} = O_2$ 5.2 (2) μM, CO 1.3 (2) μM;[z] $n = O_2$ 1.39 (4), CO 1.40 (8)	484
water snake Hb (3 Hb components)								
H. Modestus	25	7.0	TRIS-HCl or BIS-TRIS	1.00	7.60×10^2			493
			TRIS-HCl or BIS-TRIS-HCl, 1 mM ATP	8.91	85.3			493
L. Miliaris			TRIS-HCl or BIS-TRIS-HCl	1.41	5.39×10^2			493
			TRIS-HCl or BIS-TRIS-HCl, 1 mM ATP	17.80	42.70			493
Mustelus		9					$\Delta H^\circ = -15.3$	488
Raja		9					$\Delta H^\circ = -13.7$	488
Fundulus		9					$\Delta H^\circ = -15.8$	488
HbOGI	37	7.4	0.05 M BIS-TRIS, 0.1 M NaCl, 1 mM EDTA	18.5	41.1			500
arcid clam Hb (*Scapharca inaequivalvis*) (dimers)								
HbI native	15	7.0	0.1 M phosphate	5.7	1.3×10^2	1.44		501
HbI reconst	15	7.0	0.1 M phosphate	5.7	1.3×10^2	1.45		501
proto CoHbI	15	7.0	0.1 M phosphate	79.6	9.55	1.05		501
mole Hb (*Talpa europaea*)	37	7.4	$P_{CO_2} = 4.7$ kPa	14.2	53.5			502
	37	7.4	5.3 mM DPG, $P_{CO_2} = 4.7$ kPa	21.4	35.5			502
Thynella gemmata (adendrochirote) Hb	20	7	0.05 M phosphate			1.38 (4)	$\bar{x} = 5.2$ (2) μM	484
Artemia salina (brine shrimp)								
HbI	25	8.5	0.1 M borate buffer, 0.6 M NaCl	5.34	1.42×10^2	1.6-1.9	$\Delta H^\circ = -45.2$ (4) kJ/mol	485
HbII	25	8.5	0.02 M KCl	3.7	2.1×10^2	1.6-1.9	$\Delta H^\circ = -50$ (4) kJ/mol	485
HbIII	25	8.5		1.8	4.2×10^2	1.6-1.9	$\Delta H^\circ = -22.8$ (2) kJ/mol	485
Pimelodus maculatus (freshwater catfish)	20	6.0	0.1 M phosphate buffer	10.6	71.7		$n_{max} = 2.2$ at pH 6.8	486
	20	8.5	0.1 M phosphate buffer	1.8	4.2×10^2			486
stripped Hb hemosylate								
dugong dugon (dugong) Hb	30	7.4	0.1 M phosphate buffer, 0.1 g % Hb solution	0.79	9.6×10^2			487
	30	7.0		0.84	9.0×10^2			487
	30	6.5		1.08	7.04×10^2			487
	30	6.0		0.99	7.7×10^2			487
fish Hb								
Arapaima		~9					$\Delta H^\circ = -14.6$	488
Lepidosiren		~9					$\Delta H^\circ = -15.3$	488
Osteoglossum		~9					$\Delta H^\circ = -15.7$	488
Serrasalmus		~9					$\Delta H^\circ = -13.7$	488

TABLE XXXIV (*Continued*)

protein	T, °C	pH	other conditions	$P_{1/2}$, torr	$P_{1/2}^{-1}$, atm^{-1}	n^a	other constants	ref
seal Hb (2 components) *Leptonychotes weddelli*								
HbF (fast)	37	7.0	0.05 M HEPES buffer, 2,3-DPG:Hb = 2:1 (mole/mole)	8.0	95			494
HbS (slow)	37	7.0	0.05 M HEPES buffer, 2,3-DPG:Hb = 2:1 (mole/mole)	6.9	1.1×10^2			494
F&S	37	7.0	0.05 HEPES buffer, 2,3-DPG:Hb = 2:1 (mole/mole)	7.6	1.0×10^2			494
opossum Hb *Didelphius marsupialis*	20	7.35	0.05 M BIS-TRIS, 0.1 M NaCl	8.3	92	2.46 (0.03)	$\Delta \log P_{50}$/pH 0.63	495
	20	7.0	0.05 M BIS-TRIS, 0.1 M NaCl, IHP:heme = 10:1	30.6	24.8			495
	20	7.0	0.1 M phosphate	11.6	65.5			495
enoplobranchus Hb	20	?	0.05 M BIS-TRIS				$K = 0.4 \times 10^6$ M^{-1}, $\Delta H^\circ = -13.3$ kcal mol^{-1}	498
amphitrite Hb	20		0.05 M BIS-TRIS				$K = 0.2 \times 10^6$ M^{-1}	498
leghemoglobin	20	6.5	0.5 M BIS-TRIS	0.047	1.6×10^4			460
	25	6.5	0.1 M phosphate	0.045	1.7×10^4			460
	20	7.0	0.7 M ionic strength (potassium phosphate)	0.050	1.5×10^4			461
leghemoglobin a	20	7.0	0.7 M ionic strength (potassium phosphate)	0.040	1.9×10^9			461
leghemoglobin c	20	7.0	0.7 M ionic strength (potassium phosphate)	0.068	1.1×10^4			461
leghemoglobin d	20	7.0	0.7 M ionic strength (potassium phosphate)	0.063	1.2×10^4			461
			B. Myoglobins					
Mb		7.0	0.2 M phosphate buffer	0.52	1.5×10^3		$\Delta G^\circ = -0.4$ kcal mol^{-1}, $\Delta H^\circ = -14.8$ kcal mol^{-1}, $\Delta S^\circ = -49$ eu	396
CoMB		6.0	phosphate buffer				$K_{O_2} = 1.2 \times 10^4$ M^{-1}	396
Co protoporphyrin Mb^w	22-23	7.0	0.1 M phosphate buffer	50	15	1.0		446
	23.6	7.0	0.1 M phosphate buffer				$K_{O_2} = 2.0\ (1) \times 10^{-2}$ torr^{-1},[y] $\Delta G^\circ = 2.30$ kcal mol^{-1}, $\Delta H^\circ = -11.9$ kcal mol^{-1}, $\Delta S^\circ = 48$ eu[u]	403
Co mesoporphyrin Mb^w	22-23	7.0	0.1 M phosphate buffer	50	15	1.0		446
	22.8	7.0	0.1 M phosphate buffer				$K_{O_2} = 2.0\ (1) \times 10^{-2}$ torr^{-1},[y] $\Delta G^\circ = 2.30$ kcal mol^{-1}, $\Delta H^\circ = -10.3$ kcal mol^{-1}, $\Delta S^\circ = -43$ eu[u]	403
Co deuteroporphyrin Mb^w	22-23	7.0	0.1 M phosphate buffer	20	38	1.0		446
	24.4	7.0	0.1 M phosphate buffer				$K_{O_2} = 5.0\ (2) \times 10^{-2}$ torr^{-1},[y] $\Delta G^\circ = -1.76$ kcal mol^{-1}, $\Delta H^\circ = -10.3$ kcal mol^{-1}, $\Delta S^\circ = -40$ eu[u]	403
Sulf Mb	5	8.0		530	1.4			480
horse heart Mb	20-21	7.4	0.1 M phosphate buffer	0.56	1.4×10^3			511
	33	7.4	0.1 M TRIS buffer	1.03	7.38×10^2			510
mesoheme-horse Mb^w								
covalently bound	23	7.4	0.1 M TRIS buffer	0.62 (4)	1.2×10^3			510
noncovalently bound	23	7.4	0.1 M TRIS buffer	0.69 (5)	1.1×10^3			510

native horse Mb	24	7.0		1.2	6.3×10^3			474
reconstituted proto horse Mb	24	7.0		1.03	7.38×10^2			474
meso horse Mb	24	7.0		0.54	1.4×10^3	1.0		474
deutero horse Mb	24	7.0		0.21	3.6×10^2	1.0		474
hemato horse Mb	24	7.0		1.2	6.3×10^2	1.0		474
proto monoester horse Mb	24	7.0		1.2	6.3×10^2	1.0		474
proto diester horse Mb	24	7.0		1.06	7.17×10^2	1.0		474
horse heart								
2,4-diformyldeutero Mb	25	7.0	0.1 M phosphate buffer	2.8	2.7×10^2		$\Delta H^\circ = -15.5$ kcal/mol, $\Delta S^\circ = -37.8$ eu	477
spirographis Mb	25	7.0	0.1 M phosphate buffer	2.7	2.8×10^2		$\Delta H^\circ = -15.5$ kcal/mol, $\Delta S^\circ = -37.8$ eu	477
isospirographis Mb	25	7.0	0.1 M phosphate buffer	1.0	7.6×10^2		$\Delta H^\circ = -14.3$ kcal/mol, $\Delta S^\circ = -31.7$ eu	477
protopor Mb	25	7.0		1.0	7.6×10^2		$\Delta H^\circ = -14.3$ kcal/mol, $\Delta S^\circ = -31.7$ eu	477
horse CoMb	25	6.9	0.1 M phosphate buffer	57	13		$\Delta G^\circ_{25} = 2.4$ kcal mol^{-1}, $\Delta H^\circ = -11.3$ (5), kcal mol^{-1}, $\Delta S^\circ = -46$ (1.5) eu[u]	464
Apylsia Mb				2.7	2.7×10^2			448
Co Mb(Aplysia) with								
proto	4	7.0	0.1 M phosphate buffer	330	2.3			473
meso	4	7.0	0.1 M phosphate buffer	420	1.8			473
deutero	4	7.0	0.1 M phosphate buffer	210	3.6			473
proto FeMb (*Aplysia*)	15	7.0	0.1 M phosphate buffer	1.35	5.63×10^2			473
sperm whale CoMb	30	6.9	0.1 M phosphate buffer	90	8.4		$\Delta G^\circ_{30} = 2.7$ kcal mol^{-1}, $\Delta H^\circ = -12.7$ (5) kcal mol^{-1}, $\Delta S^\circ = -51$ (3) eu[u]	463
	25	6.9	0.1 M phosphate buffer	57	13		$\Delta G^\circ_{25} = 2.4$ kcal mol^{-1}, $\Delta H^\circ = -13.3$ (5) kcal mol^{-1}, $\Delta S^\circ = -53$ (1.5) eu[u]	464
			C. Chlorocruorin					
Spirographus spallanzanii	20	7.5	CHL 5 mg/mL, 0.1 M TRIS		3.2		$\log P_{1/2} = 1.6$	466
(chlorocruorin = CHL)	20	7.5	CHL 5 mg/mL, 0.3 M TRIS		3.6		$\log P_{1/2} = 1.60$, $\Delta H^\circ = -4.5$ kcal/mol (incl. oxygenation, $\Delta H^\circ_{\text{solution}}O_2$, subunit interaction)	466
	20	7.5	CHL 5 mg/mL, 0.1 M TRIS, 0.3 M NaCl		3.5		$\log P_{1/2} = 1.55$	466
	20	7.5	CHL 5 mg/mL, 0.1 M TRIS, 0.6 M NaCl		3.8		$\log P_{1/2} = 1.44$	466
	20	7.5	CHL 5 mg/mL, 0.1 M TRIS, 1.5 M NaCl		3.9		$\log P_{1/2} = 1.21$	466
	20	7.5	CHL 5 mg/mL, 0.1 M TRIS, 3.0 M NaCl		3.5		$\log P_{1/2} = 0.91$	466
			D. Hemocyanins					
Callianassa californiensis	25	7.65	TRIS buffer	100	7.6	1.28		469
(ghost shrimp) Hcy	25	7.65	TRIS buffer, 0.025 M Mg^{2+}	42	18	2.90		469
	25	7.65	TRIS buffer, 0.050 M Mg^{2+}	26	29	3.25		469
	25	7.8	TRIS buffer, 0.050 M Ca^{2+}	14	54			469
	25	7.00	TRIS buffer, 0.05 M Mg^{2+}, 0.01 M Ca^{2+}	132	5.76	1.14		469
	25	7.65	TRIS buffer, 0.05 M Mg^{2+}, 0.01 M Ca^{2+}	21	3.6	3.07		469

TABLE XXXIV (*Continued*)

protein	T, °C	pH	other conditions	$P_{1/2}$, torr	$P_{1/2}^{-1}$, atm^{-1}	n^a	other constants			ref
	25	8.00	TRIS buffer, 0.05 M Mg^{2+}, 0.01 M Ca^{2+}	6.6	1.2×10^2	3.33				469
	3	7.8	TRIS buffer, 0.05 M Mg^{2+}, 0.01 M Ca^{2+}	9.0	84					469
	16	7.8	TRIS buffer, 0.05 M Mg^{2+}, 0.01 M Ca^{2+}	7.0	1.1×10^2					469
	25	7.8	TRIS buffer, 0.05 M Mg^{2+}, 0.01 M Ca^{2+}	14.0	54.3					469
Jasus lalandii hemocyanin	20	8.0		~8[aa]	~100					459
	20	6.5		~6[aa]	~100					459
	20	5.5		~4[aa]	~200					459
Levantina hierosolima (snail) hemocyanin	15.0	8.2	0.1 M TRIS-HCl, 0.3 mg of Hcy/mL	3.1	2.5×10^2					489
	20.6	8.2	0.1 M TRIS-HCl, 0.3 mg of Hcy/mL	4.3	1.8×10^2					489
	25.0	8.2	0.1 M TRIS-HCl, 0.3 mg of Hcy/mL	4.9	1.6×10^2					489
	31.0	8.2	0.1 M TRIS-HCl, 0.3 mg of Hcy/mL	7.8	97					489
	40.0	8.2	0.1 M TRIS-HCl, 0.3 mg of Hcy/mL	14.1	53.9					489
						[ab]form	reaction	ΔG°, kcal/mol^{-1}	ΔH°, kcal/mol	ΔS°, eu	
	15.0	8.2	0.1 M TRIS-HCl, 0.3 mg of Hcy/mL, 0.02 M Ca^{2+}	9.4	81	N	oxygenation	−6.960	−7.460	−1.7	489
	20.0	8.2	0.1 M TRIS-HCl, 0.3 mg of Hcy/mL, 0.02 M Ca^{2+}	8.1	94	L	oxygenation	−6.030	+3.050	30.5	489
	25.0	8.2	0.1 M TRIS-HCl, 0.3 mg of Hcy/mL, 0.02 M Ca^{2+}	10.2	74.3	H	oxygenation	−6.930	−7.460	−1.8	489
	32.0	8.2	0.1 M TRIS-HCl, 0.3 mg of Hcy/mL, 0.02 M Ca^{2+}	12.7	59.8		site interaction	−0.910	−11.000	−33.9	489
	40.0	8.2	0.1 M TRIS-HCl, 0.3 mg of Hcy/mL, 0.02 M Ca^{2+}	11.9	63.9						489
Panulirus interruptus (spiny lobster) Hcy	20	7.22	0.05 M TRIS-HCl, 10 mM $CaCl_2$, μ = 0.13	38	20		1.96				490
	20	7.43	0.05 M TRIS-HCl, 10 mM $CaCl_2$, μ = 0.13	34	22		2.05				490
Ligia exotica (marine) isopod Hcy											
hexamer	20	9.0	0.1 M TRIS, 0.1 M NaCl	1.02	7.45×10^2		3.2				483
monomer	20	9.5		1.37	5.55×10^2		1.2				483
Lymnaea stagnalis (snail) Hcy	20	6.8	10 mM HEPES, 5 mM $CaCl_2$	7.24	1.05×10^2		2.3				567
	20	6.8	10 mM HEPES, 10 mM $CaCl_2$	5.01	1.52×10^2		2.0				567
	20	6.8	10 mM HEPES, 20 mM $CaCl_2$	4.57	1.66×10^2		2.3				567
	20	7.2	10 mM HEPES, 10 mM $CaCl_2$	3.09	2.46×10^2		2.2				567
	20	7.5	10 mM HEPES, 10 mM $CaCl_2$	2.75	2.76×10^2		3.5				567
	20	7.5	10 mM HEPES, 10 mM $CaCl_2$, 5 mM NaCl	2.05	3.71×10^2		3.5				567
	20	7.5	10 mM HEPES, 10 mM $CaCl_2$, 50 mM NaCl	4.45	1.71×10^2		8.6				567
	20	7.6	10 mM HEPES, 10 mM $CaCl_2$, 0 mM NaCl	1.99	3.82×10^3		2.4				567

Penacus setiferus	20	6.63	50 mM TRIS buffer, 10 mM $CaCl_2$	112	6.79	3.1		468
(shrimp) Hcy	20	7.60	50 mM TRIS buffer, 10 mM $CaCl_2$	24	32	4.0	other pH's omitted	468
	20	8.20	50 mM TRIS buffer, 10 mM $CaCl_2$	3.3	2.3×10^2	3.3		468
	20	9.10	50 mM TRIS buffer, 10 mM $CaCl_2$	0.3	3×10^3	2.8		468
	20	8.2	50 mM TRIS buffer, 10 mM $CaCl_2$, 0.1 M [Cl^-]	3.3	2.3×10^2	4.2		468
	20	8.2	50 mM TRIS buffer, 10 mM $CaCl_2$, 0.5 M [Cl^-]	1.1	6.9×10^2	3.7	other pH's omitted	468
	20	8.2	50 mM TRIS buffer, 10 mM $CaCl_2$, 2.0 M [Cl^-]	0.2	4×10^3	2.2		468
	20	7.85	50 mM TRIS buffer, 0 mM $CaCl_2$	10.5	72.4	4.0		468
	20	7.85	50 mM TRIS buffer, 5 mM $CaCl_2$	8.3	92	3.7		468
	20	7.85	50 mM TRIS buffer, 10 mM $CaCl_2$	5.6	1.4×10^2	4.2		468
	20	7.85	50 mM TRIS buffer, 20 mM $CaCl_2$	3.2	2.4×10^2	4.0		468
			E. Hemerythrin					
Sipunculus nudus	20	6.25	unbuffered	2.9	2.6×10^2			458
hemerythrin	20–21	7.4	0.1 M phosphate buffer	2.2	3.5×10^2			511
	25	6–9.5[ac]	buffer not specified				$K_{O_2} = 1.0 \times 10^5\ M^{-1}$, $\Delta H^\circ = -13.5$ kcal mol^{-1}	

[a] Hill's n is a measure of cooperativity of O_2 binding. [b] P_m = median ligand activity (see ref 445a). [c] Larger than previous (ref 439) due to small amounts of phosphate compounds in the sample. [d] K_T and K_R are equilibrium constants calculated for uptake of O_2 by the Hb in the tense (T) and relaxed (R) states, respectively, of the Monod model for Hb oxygenation. [e] C_A = concentration of alcohol (v/v × 100). [f] Based on 4 log Psa(C_A)/Psa(O) = log $L(C_A)/L(O)$, where L = ratio of T state to R state in absence of O_2. [g] Phosphate compounds generally decrease the O_2 affinity of Hb. Organisms sometimes take advantage of this fact in regulating oxygen release by erythrocytes. [h] Thermodynamic values at 25 °C determined for calorimetric data at 6 °C assuming the temperature dependence of the enthalpies is 0. [i] Reference 468a. [j] Standard state of 1 atm of O_2. [k] Estimated values. [l] NES β has *N*-ethylsuccinamide attached to CYS 93β, preventing salt bridge formation between ASP 94β and HIS 146β. [m] Fetal hemoglobin. [n] Free SH groups have been regenerated on the chains. [o] This designation, here and elsewhere, indicates that the designated porphyrin complex has been combined with the apoprotein to form a modified protein containing abnormal porphyrin. [p] Calculated per mol of O_2 and half-saturation. [q] The cyanomet form of the designated chain has been formed by reaction of this chain with $KCN/K_3FE(CN)_6$. [r] The protein has been treated with carboxypeptidase A (CPA), iodoacetamide (IAA), or *N*-ethylmaleimide (NME). [s] β^{PMB} has the sulfhydryl groups blocked with *p*-chloromercuribenzoate. [t] Superscript –PMB indicates sulfhydryl groups blocked with *p*-chloromercuribenzoate, superscript –SH indicates that free sulfhydryl groups have been regenerated. [u] Standard state of 1 torr of O_2. To convert to 1-atm standard state, add 13.2 L eu; –58.1 eu at 1-torr standard state becomes –44 eu at 1-atm standard state. [v] $K_{O_2} = (P_{1/2})^-$ for Hb and Mb prior to 1970; see ref 26. For abnormal Hb's, see ref 495 and 496. [w] See footnote *o*. [x] Determined from kinetic measurements. [y] Catalase added in trace amounts to prevent buildup of H_2O_2. [z] $\bar{x}$ = half-saturation ligand activity. [aa] Data given in graphical form only. These constants were read directly from the graph. [ab] Noncooperative in absence of Ca^{2+}, cooperative with Ca^{2+} present, low affinity (L) at high affinity (H) forms. [ac] No Bohr effect observed.

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(53) This term is used in preference to the term "dioxygen carriers" for the sake of brevity and to comply as closely as possible to current scientific usage.
(54) A model, in this context, is a relatively simple and well-characterized compound or system which mimics some of the properties of a biological compound or system. Thus a simple iron-porphyrin compound is a model for hemoglobin. Examples of model compounds may be found in refs 2–15, 29–31.
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