

distorts or the  $ML_2$  unit slips to a lower coordination number.<sup>21,27b,31</sup>

### Conclusions and Extensions

No matter which way one dissects these barriers, it is the electronic asymmetry at the metal (tailored by the other ligands) that causes them. There is a threefold pattern for  $C_{3v}$   $ML_3$  complexes and a twofold one in the  $C_{2v}$   $ML_2$  and  $C_{2v}$   $ML_4$  compounds. A  $\delta$  orbital can also create a barrier for a  $C_{4v}$   $ML_4$  or  $C_{4v}$   $ML_5$  complex (the  $a_2$  orbital for  $C_{4v}$   $ML_4$  in Figure 4).<sup>27</sup> We have neglected steric effects in this review. They are minimal for the cases presented here, but this is not always the case. The orientation and the source of rotational barriers in the Zeise's salt complexes, **3**, are actually set by steric factors.<sup>27a,32</sup> It takes something as large as a *tert*-butyl group on, for example, a benzene ring to cause an appreciable effect on the rotational potential for a compound where there is normally a small barrier.<sup>23,33</sup> In systems possessing a much larger barrier such as the acyclic polyene- $ML_3$  class there are a number of examples<sup>34</sup> where extremely close contacts exist between substituents on the polyene ring and the

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L groups in the electronically favored conformation **26**. The steric problems could have been relieved by rotation to **27**, but structural studies still find **26** as the ground state conformation.

The fragment orbital analysis of rotational barriers can be extended to transition-metal dimers and trimers.<sup>35</sup> It is easy to see how a barrier from  $L_3M-ML_3$  or  $L_4M-ML_4$  complexes can be created. There are a large number of other fragments that can be considered; each have specific electronic properties. One particularly nice example is given by  $CpML_2$  complexes of polyenes.<sup>36</sup> It can be shown that the regioselectivity of attack by nucleophiles on  $CpMo(CO)(NO)(allyl)^+$  is determined by the orientation of the allyl ligand with respect to the  $CpMLL'$  unit.<sup>36b</sup> The many coordination geometries available to transition metals and the countless ways that electronic perturbations can be incorporated make this an exciting field where there is still much work to be done.

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## Formation and Stabilities of Cobalt Dioxygen Complexes in Aqueous Solution<sup>†</sup>

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The earliest known synthetic dioxygen complex is probably  $[(NH_3)_{10}Co_2O_2]^{4+}$ , described by Werner and Myelius in 1893,<sup>1</sup> but this discovery was not pursued further until the report by Tsumaki<sup>2</sup> on the properties of the cobalt(II) chelate of bis(salicylal)ethylenediamine, "salcomine". This development was followed by a period of activity involving three research groups. Calvin and co-workers<sup>3-9</sup> published a series of papers on the properties of the salcomine-type chelates in 1946-1947, and a series of papers on similar compounds by Diehl and co-workers<sup>10</sup> appeared at about the same time. Much of the early incentive for investigating the

salcomine-type oxygen-carrying chelates was to develop a practical system of preparing pure oxygen from gaseous mixtures with light-weight equipment. Recently, the fluorine-substituted salcomine chelate, "fluomine", has been employed as the basis of a successful oxygen supply system.<sup>11-14</sup> Further interest in cobalt dioxygen

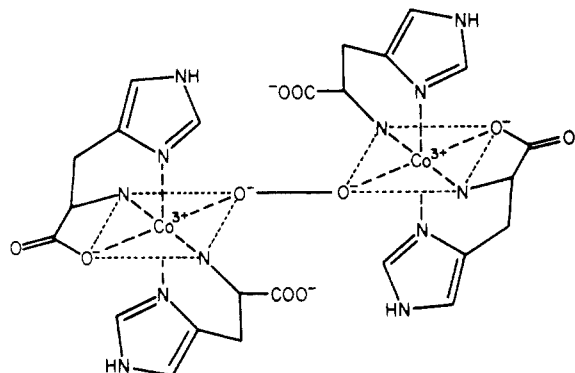
<sup>†</sup>This paper is an updated version of a presentation made at the 179th National Meeting of the American Chemical Society, March 24, 1980, on the occasion of the ACS Award for Distinguished Service in the Advancement of Inorganic Chemistry, sponsored by Mallinckrodt, Inc.

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complexes has developed as models for binuclear oxygen-carrying and oxygen-storage proteins and as catalysts for direct reduction of oxygen to water in homogeneous solution and on electrode surfaces.

The first equilibrium studies of cobalt dioxygen complex formation were reported for bis(histidinato)-cobalt(II) by Burk, Hearon, and co-workers.<sup>15-18</sup> The coordinate bonding in the binuclear dioxygen complex, indicated by formula 1, is considered different from that



1, bis(histidinato)cobalt(II) dioxygen complex

suggested originally. The dioxygen is represented as a peroxy bridge between two cobalt(III) atoms, in conformity with the diamagnetism of the compound, as well as with the O-O bond distances that have been determined for a number of similar binuclear cobalt dioxygen complexes.

### Mononuclear vs. Binuclear Dioxygen Complex Formation

Although Calvin<sup>3,5</sup> had designed a ligand that would promote the formation of a 1:1 (mononuclear) cobalt(II) dioxygen complex in the solid state, most of the mononuclear dioxygen complexes of cobalt(II) have been discovered only recently. Basolo and co-workers<sup>19,20</sup> found that under suitable conditions (i.e., in a donor solvent of relatively low dielectric constant) [*N,N'*-ethylenebis(salicylaldiminato)]cobalt(II) and [*N,N'*-ethylenebis(acetylacetonimine)]cobalt(II) form 1:1 (mononuclear) dioxygen complexes. Mononuclear dioxygen complexes are also formed under appropriate conditions by a number of macrocyclic ligands such as vitamin B<sub>12</sub>,<sup>21</sup> protoporphyrin IX dimethyl ester,<sup>22,23</sup> and tetrasulfophthalocyanine.<sup>24,25</sup> Collman<sup>26</sup> has dem-

onstrated the value of hydrophobic substituents in stabilizing the cobalt(II)-dioxygen bond. Of special interest is coboglobin,<sup>27</sup> a reconstituted hemoglobin in which a cobalt(II) protoporphyrin IX complex replaces the heme. Considerable work on its dioxygen complex has been reported recently.<sup>28-33</sup>

Formation of binuclear cobalt(II) dioxygen complexes requires the formation of mononuclear 1:1 complexes as intermediates. The conditions favoring the formation of mononuclear complexes are based either on stabilization of the mononuclear species or on inhibition of the formation of the binuclear form. Such factors are low concentration, low temperature, use of a low dielectric constant medium, and steric hindrance. Since binuclear, peroxy-bridged binuclear dioxygen complexes have more polar metal-oxygen coordinate bonds than the mononuclear (superoxo) complexes, it is reasonable that the latter are favored in solvents of low dielectric constant. The attachment of the coordinated metal center to a macromolecule, in which there is little opportunity for two coordinated metal ions to combine with a single dioxygen molecule, favors mononuclear dioxygen complex formation, as exemplified by hemoglobin and myoglobin and by synthetic oxygen carriers consisting of iron(II) tetraphenylporphyrin attached to a modified silica gel support<sup>34</sup> on iron(II) protoporphyrin bonded to water-soluble polymers.<sup>35</sup> Collman's "picket-fence" cobalt(II) and iron(II) porphyrin derivatives,<sup>26,36</sup> are examples of the lengths to which it is necessary to go in employing steric effects to prevent binuclear dioxygen complex formation (which in the case of iron(II) would lead to rapid autoxidation and formation of the inert iron(III)  $\mu$ -oxo dimer). The "picket-fence" complex and the Baldwin<sup>37</sup> "capped" iron(II) porphyrin complex are among the most successful hemoglobin model systems developed thus far, combining reversibly with dioxygen to form 1:1 superoxo complexes at or near room temperature.

Further information on dioxygen complexes is available from the many excellent reviews on this subject. The early work on oxygen-carrying cobalt chelates was summarized by Martell and Calvin.<sup>38</sup> The formation and properties of oxygen complexes of a wide

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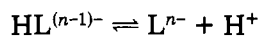
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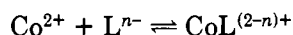
variety of transition metals have been reviewed by Vaska,<sup>39</sup> Collman,<sup>40</sup> Taube,<sup>41</sup> Valentine,<sup>42</sup> Taqui Khan and Martell,<sup>43</sup> Wilkins,<sup>44</sup> Vogt et al.,<sup>45</sup> Basolo et al.,<sup>46</sup> McLendon and Martell,<sup>47</sup> Jones et al.,<sup>48</sup> and Timmons et al.<sup>49</sup>

### Oxygenation Equilibria in Aqueous Solution

The equilibria involved in the formation of cobalt dioxygen complexes in aqueous solution<sup>47</sup> are indicated by eq 1-7. The multidentate ligand, L, is generally very

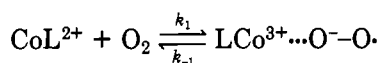


$$K^{\text{H}}_{\text{L}} = [\text{HL}^{(n-1)-}] / [\text{H}^+][\text{L}^{n-}] \quad (1)$$

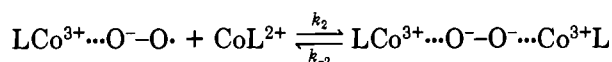


$$K_{\text{f}} = [\text{CoL}^{(2-n)+}] / [\text{Co}^{2+}][\text{L}^{n-}] \quad (2)$$

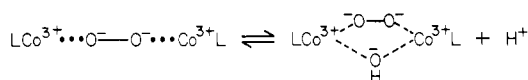
for  $n = 0$



$$K_{11} = [\text{LCoO}_2^{2+}] / [\text{CoL}^{2+}][\text{O}_2] \quad (3)$$



$$K_{12} = [\text{L}_2\text{Co}_2\text{O}_2^{4+}] / [\text{LCoO}_2^{2+}][\text{CoL}^{2+}] \quad (4)$$



$$K_{\text{a}} = \frac{[\text{L}_2\text{Co}_2\text{O}_2\text{OH}^{3+}][\text{H}^+]}{[\text{L}_2\text{Co}_2\text{O}_2^{4+}]} \quad (5)$$

$$K_{\text{O}_2} = [\text{Co}_2\text{L}_2\text{O}_2^{4+}] / [\text{CoL}^{2+}]^2[\text{O}_2] \quad (6)$$

$$K'_{\text{O}_2} = [\text{Co}_2\text{L}_2\text{O}_2\text{OH}^{3+}][\text{H}^+] / [\text{CoL}^{2+}]^2[\text{O}_2] \quad (7)$$

basic and undergoes a series of protonation reactions in solution over a range of pH. Equation 1 illustrates only the last dissociation step at high pH, corresponding to the first protonation equilibrium constant. Combination of cobalt(II) with the ligand and the successive reactions of the resulting cobalt complex with dioxygen are indicated by eq 2-4. Although hydrogen ions are not involved in these equilibria, the reactions are actually highly hydrogen ion dependent in aqueous solution. It is well-known that cobalt(II) complexes begin to form at pH values considerably below the pH at which the ligand is completely deprotonated. Thus

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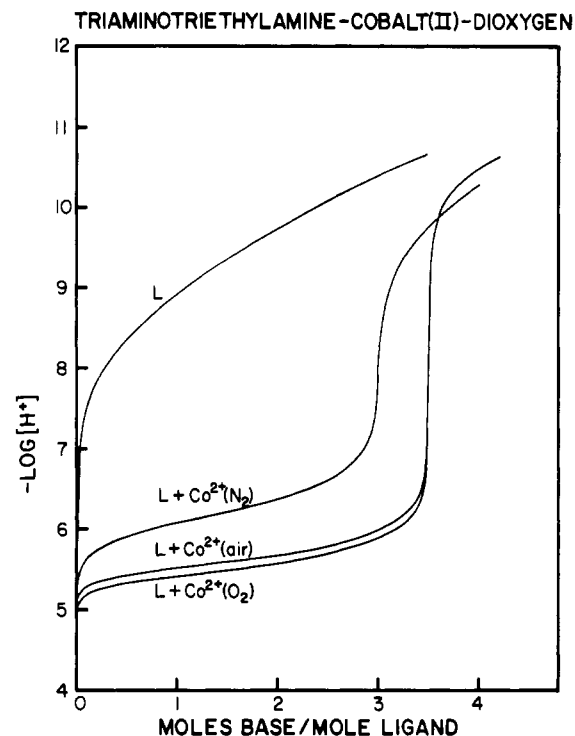
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**Figure 1.** Potentiometric equilibrium curves for the system triaminotriethylamine (TREN) trihydrochloride-cobalt(II)-dioxygen. L = ligand under nitrogen in absence of metal ion; L + Co<sup>2+</sup>(N<sub>2</sub>) = equimolar ratio of Co(II) and TREN under nitrogen; L + Co<sup>2+</sup>(air) = equimolar ratio of Co(II) and TREN under air at 1.00 atm; L + Co<sup>2+</sup>(O<sub>2</sub>) = equimolar ratio of Co(II) and TREN under oxygen at 1.00 atm; T<sub>M</sub> = T<sub>L</sub> = 1.000 × 10<sup>-3</sup> M; t = 25 °C; μ = 0.100 M (KNO<sub>3</sub>).

reactions 2-4 overlap with 1 as well as with reactions involving higher degrees of protonation of the ligand, and the oxygenation constants involved may be readily determined potentiometrically. The mononuclear complex indicated in eq 3 has been inferred from kinetic measurements,<sup>44,47,50</sup> but discussion of such evidence is beyond the scope of this Account. In practice, dioxygen complex formation in aqueous solution does not stop at the mononuclear complex stage, and one generally sees a single buffer region in which the cobalt(II) ion and the protonated ligand are converted to the binuclear dioxygen complex.

When the ligand L is pentadentate and formation of the dioxygen complex completes the coordination sphere of the cobalt(III), eq 4 represents the termination of the oxygenation process. On the other hand, when the ligand L does not supply a sufficient number of donor groups to completely coordinate the metal (i.e., when one or more aquo donor groups remain in the coordination sphere of the cobalt(III)), the oxygenation process is usually accompanied by the hydrolysis of coordinated water to form a hydroxo bridging group (eq 5) although exceptions have been noted.<sup>51</sup> This reaction is hydrogen ion dependent and requires an additional half equivalent of base to complete the process. It is convenient to express the oxygenation constant in terms of the formation of the dioxygen complex from the fully formed Co(II) complex by employing eq 6 for pentadentate ligands and eq 7 for ligands that supply less than five strongly coordinating donor groups to the metal ion.

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### Stabilities of Dibringed Cobalt Dioxygen Complexes

Typical behavior for the formation of a cobalt dioxygen complex in aqueous solution is illustrated by the potentiometric equilibrium curves in Figure 1.<sup>52</sup> In this system the ligand L, triaminotriethylamine, was introduced as the trihydrochloride and is seen to have a neutralization curve at high pH corresponding to the presence of three strongly basic donor groups with pK values ranging from about 8 to 10. In the presence of an equimolar amount of Co(II) under an inert atmosphere, the strong depression of the potentiometric equilibrium curve to lower pH values indicates strong binding between the metal ion and the tetradentate ligand. The inflection at 3 mol of base/mole of ligand demonstrates the stoichiometry of complex formation, and the depression of the buffer region provides qualitative evidence for the stability of the complex.

The potentiometric data in Figure 1 provide valuable evidence about the nature of the dioxygen complex formed. The inflection at a neutralization value of 3.5 indicates the stoichiometry of the complex formation reaction, and the presence of a single hydroxide bridge in the binuclear dioxygen complex. The fact that the buffer region involving the formation of the dioxygen complex occurs at lower pH values when the pressure of the dioxygen is increased demonstrates that the displacement of hydrogen ion from the ligand is sensitive to the concentration of dioxygen and demonstrates that equilibrium data may be employed to calculate the overall formation constant of the dioxygen complex from metal ion, protonated ligand, and molecular oxygen. Further, the considerable additional depression of the buffer region caused by the presence of dioxygen indicates that combination of oxygen with metal ion somehow greatly increases the affinity of the metal ion for the basic nitrogen donors of the ligand, thus increasing the extent to which the metal ion displaces protons from these donor groups. The only reasonable interpretation that can be offered to explain data of this nature is that the metal ion may now be considered to be in the trivalent state and that the oxygen in the binuclear complex occurs as a peroxy-type ligand, thus accounting for the increased stability of the system as well as its diamagnetic behavior. Because of the accumulation of considerable potentiometric data of this type, members of this research group long ago (~15 years) had begun to write the formulas of binuclear cobalt dioxygen complexes so as to indicate a formally trivalent cobalt(III) ion coordinated to a peroxy bridge.

Stability constants of dibringed dioxygen complexes (defined by eq 7) are listed in Table I, together with stability constants of the Co(II) complexes from which they are formed. It is interesting that the logarithms of the oxygenation constants (or alternatively, the free energies of formation of the oxygen complexes) do not correlate in any way with the stability constants<sup>53</sup> of the corresponding Co(II) complexes. On the other hand, the oxygenation constants correlate very well with the sums of the pK values of the donor groups of the ligands that are coordinated to the cobalt(II) center.<sup>47,54</sup> This

Table I  
Correlation of Stabilities of Dibringed Dioxygen Complexes of Cobalt with Basicities of Ligands<sup>a</sup>

ligand <sup>b</sup>	$\Sigma pK$	$\log K_{ML}$	$\log K_{O_2}$
SEDDA	16.2	11.2	-4.1
UEDDA	16.7	11.6	-5.3
SDTMA	25.3	12.3	2.3
UDTMA	24.6	12.1	2.4
DIEN	23.2	8.2	1.1
TRIEN	28.7	10.4	6.1
TREN	30.5	12.3	4.4
(EN) <sub>2</sub>	35	10.7	10.8
(His) <sub>2</sub>	32	9.0	8.5
HEDIEN	22.5	7.9	1.5

<sup>a</sup> All measurements made at  $25 \pm 0.1^\circ\text{C}$ ;  $\mu = 1.0\text{ M}$  ( $\text{KNO}_3$ );  $\Sigma pK$  is summation of the pK values of all donor groups coordinated to cobalt;  $K_{ML}$  values are cobalt(II) chelate stability constants. <sup>b</sup> Abbreviations defined in ref 56.

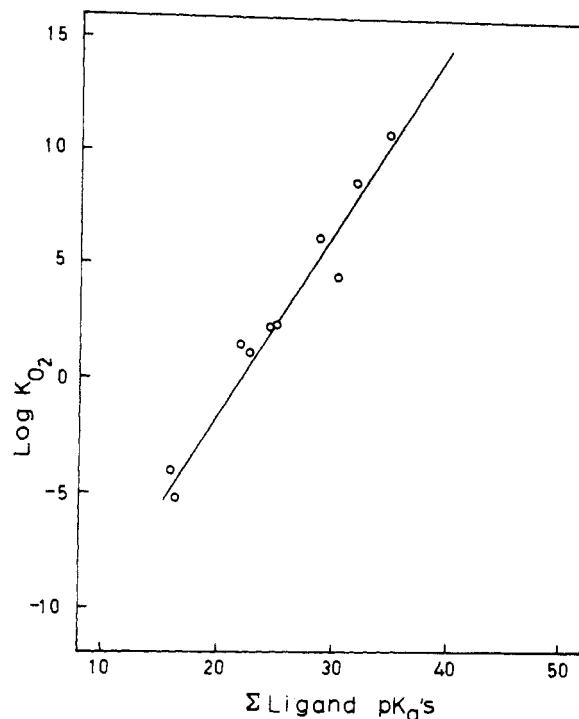


Figure 2. Correlation of  $\log K_{O_2}$  of dibringed dioxygen complexes with the sum of the log protonation constants of the ligands; values of  $\log K_{O_2}$  and sum of ligand pK<sub>a</sub> values taken from Table I.

correlation is illustrated in Figure 2, which indicates a linear relationship over 15 orders of magnitude of the oxygenation constants. This linear correlation probably cannot be extended much beyond the range of  $\log K$  values and ligand pK values indicated in Figure 2. A larger number of donor groups of high basicity, or a similar number with higher basicity, would be difficult to obtain for the type of oxygen complex under consideration without exceeding the limitation of four-coordination of the metal ion. At the lower stability end it should be possible to extend the correlation to somewhat lower pK values through the use of aromatic amines such as pyridine, bipyridyl, *o*-phenanthroline, with the limitation that four-coordination not be exceeded. The lower limit is of course governed by the fact that some basicity must be maintained in the ligands to form stable Co(II) complexes. It should be pointed out that  $\log K_{O_2}$  values of -5 or lower represent

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complexes having reasonable stability in aqueous solution. The equilibrium quotient in eq 7 indicates that at pH 7, for example, the dioxygen complex is nearly completely formed.

The data in Table I and Figure 2 indicate that it is not necessary to have three or more basic nitrogen donors in order to form stable dioxygen complexes in aqueous solution. This violation of the "3 nitrogen" rule advanced by Fallab<sup>55</sup> is due to the stabilizing influence of the hydroxo bridge. Without this additional bridge the complexes formed from ligands with only two basic nitrogen donor groups would probably be highly dissociated. Another implication of the correlation in Figure 2 is that it is now possible to form cobalt dioxygen complexes in aqueous solution of predetermined stability over a wide range of possible values by merely selecting coordinating ligands with donor groups of the required basicities, so that the sum of the pK values would have the value indicated by the correlation. It should be pointed out that the use of the pK sum for predicting stabilities of dioxygen complexes is an indication that coordination of the dioxygen by cobalt involves primary  $\sigma$  bonds, in conformity with the formalism described above in which the metal ion is represented as Co(III) and the oxygen is designated as a coordinated  $\mu$ -peroxo ligand.

### Influence of Ligand Basicity on Stabilities of Mononuclear Dioxygen Complexes

It is of interest to compare the correlation described above with a similar correlation described by James et al.<sup>57</sup> and Jones et al.<sup>48</sup> For the dioxygen complexes under consideration, the main ligand, protoporphyrin IX dimethyl ester (PPIXDME), is a constant factor and differences in stability are achieved by varying the basicity of the axial base. Since the coordinated superoxo group has a vacant p orbital, its affinity for the metal ion varies with both the  $\sigma$ -bonding and  $\pi$ -bonding effects to the axial base. A linear correlation with pK<sub>a</sub> was observed with pyridine derivatives, for which changes in  $\pi$  bonding to dioxygen resulting from  $\pi$ -donor effects of the axial ligand remain relatively constant, and the variation is mainly the result of changes in  $\sigma$  bonding. When imidazolyl derivatives are employed as axial bases, their stabilities lie above the linear correlation for the pyridine derivatives, in accordance with the fact that imidazole is a better  $\pi$  donor than pyridine.<sup>48</sup> Similarly the stability constant obtained with the aliphatic base piperidine reflects the lack of  $\pi$ -donor effects on the part of this ligand.

(55) S. Fallab, *Angew. Chem., Int. Ed. Engl.*, 6, 496 (1967).

(56) Abbreviations or acronyms for ligands discussed in this paper, in sequence presented, are as follows: SEDDA, *N,N'*-ethylenediaminediacetic acid; UEDDA, *N,N'*-ethylenediaminediacetic acid; SDTMA, *N,N*-bis(2-aminoethyl)glycine; UDTMA, *N*-diethylenetriamineacetic acid; DIEN, diethylenetriamine; TRIEN, triethylenetetramine; TREN, 2,2',2''-tris(aminoethyl)amine; EN, ethylenediamine; HEDIEN, *N*-(2-hydroxyethyl)diethylenetriamine; TEP, tetraethylenepentamine; EPYDEN, 2,6-bis(5-(1,4-diazahexyl))pyridine; 4-IMDIEN, 1,9-bis(4-imidazolyl)-2,5,8-triazanone; PYDIEN, 1,9-bis(2-pyridyl)-2,5,8-triazanone; TRPY, 2',5'-bis(2-pyridyl)pyridine; PHEN, 1,1-phenanthroline; BPY, 2,2'-bipyridyl; 4-IMDPT, 1,11-bis(4-imidazolyl)-2,6,10-triazaundecane; 2-IMDPT, 1,11-bis(2-imidazolyl)-2,6,10-triazaundecane; PYDPT, 1,11-bis(2-pyridyl)-2,6,10-triazaundecane; BISTREN, 1,4,10,13,16,22,27,33-octaaza-7,19,30-trioxabicyclo[11.11.11]pentatriacontane; PXBDE, tetrakis(2-aminoethyl)- $\alpha,\alpha'$ -diamino-*p*-xylene; BISDIEN, 1,4,7,13,16,19-hexaaza-10,22-dioxacyclotetracosane; TPivPP, 5,5,5,5-tetrakis(*o*-(pivaloamido)phenyl)porphine; SALEN, [*N,N'*-ethylenebis(salicylaldiminato)]cobalt(II); ACACEN, [*N,N'*-ethylenebis(acetylacetonate)]cobalt(II).

(57) D. V. Stynes, H. C. Stynes, B. R. James, and J. A. Ibers, *J. Am. Chem. Soc.*, 95, 1796 (1973).

Table II  
Correlation of Stabilities of Monobridged Dioxygen Complexes of Cobalt with Basicities of Ligands<sup>a</sup>

ligand <sup>b</sup>	$\Sigma$ pK	log K <sub>ML</sub>	log K <sub>O<sub>2</sub></sub>
With Five-Membered Chelate Rings			
TEP	35.8	13.66	15.8
EPYDEN	30.6	13.99	14.7
4-IMDIEN	29.1	13.84	12.6
PYDIEN	21.6	14.73	11.4
TRPY(PHEN)	~13	6.52	6.3
TRPY(BPY)	~12	5.38	5.4
With Five- and Six-Membered Chelate Rings			
4-IMDPT	34.4	11.36	9.5
2-IMDPT	30.7	11.55	8.6
PYDPT	27.1	11.47	7.7

<sup>a</sup> All measurements at 25  $\pm$  0.1  $^{\circ}$ C;  $\mu$  = 1.0 (KNO<sub>3</sub>);  $\Sigma$  pK is summation of pK values of all donor groups of ligands coordinated to cobalt.  $K_{ML}$  are Co(II) chelate stability constants. <sup>b</sup> Ligand abbreviations defined in ref 56.

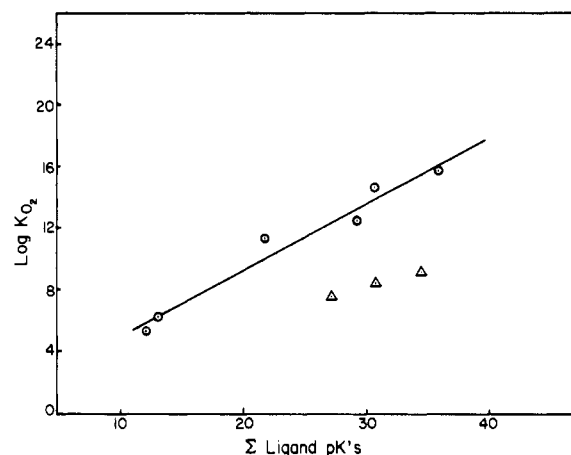


Figure 3. Correlation of log K<sub>O<sub>2</sub></sub> of monobridged dioxygen complexes with the sums of log protonation constants of the ligands: (O) complexes with five-membered chelate rings, (Δ) complexes with five- and six-membered chelate rings; values of log K<sub>O<sub>2</sub></sub> and sum of ligand pK values taken from Table 2.

### Stabilities of Monobridged Dicobalt Dioxygen Complexes

Studies of stabilities of monobridged complexes were carried out with Co(II) complexes of a series of pentadentate amines in which one or more basic nitrogen donor groups of tetraethylenepentamine is replaced by aromatic nitrogens having considerably lower basicity. The synthesis of these ligands, their affinities for various metal ions, and the oxygen affinities of their Co(II) complexes have been described.<sup>58,59</sup> The formation constants of these monobridged dioxygen complexes as well as those of several other ligands, the stability constants of the corresponding Co(II) complexes, and the sums of the pK values of the ligands are presented in Table II. Here again, oxygenation constants do not correlate with the stability constants of the corresponding Co(II) complexes but show a linear relationship with the pK sum of the ligand donor groups coordinated to the metal ion.<sup>60</sup> The stability data are separated into two groups (Figure 3): a linear correlation for pentadentate polyamines that form only five-

(58) W. R. Harris, I. Murase, J. H. Timmons, and A. E. Martell, *Inorg. Chem.*, 17, 889 (1978).

(59) J. H. Timmons, W. R. Harris, I. Murase, and A. E. Martell, *Inorg. Chem.*, 17, 2191 (1978).

(60) W. R. Harris, J. H. Timmons, and A. E. Martell, *J. Coord. Chem.*, 8, 251 (1979).

Table III  
Comparison of Bond Distances (Å) for [Co(PYDIEN)]<sub>2</sub>O<sub>2</sub><sup>4+</sup> and [Co(PYDPT)]<sub>2</sub>O<sub>2</sub><sup>4+</sup>

compd <sup>a</sup>	O-O	Co-O	N1-Co	N2-Co	N3-Co	N4-Co	N5-Co
[Co(PYDIEN)] <sub>2</sub> O <sub>2</sub> <sup>4+</sup>	1.489	1.876	1.910	2.001	1.986	1.954	1.902
[Co(PYDPT)] <sub>2</sub> O <sub>2</sub> <sup>4+</sup>	1.456	1.888 1.894	1.948 1.928	2.006 2.009	2.002 1.986	1.964 1.958	1.945 1.982

<sup>a</sup> Ligand abbreviations defined in ref 56.

Table IV  
Thermodynamics of Oxygenation of Pentacoordinated Cobalt(II) Polyamine Complexes

ligand	log K <sub>ML</sub>	ΔH <sub>ML</sub> <sup>b</sup>	TΔS <sub>ML</sub> <sup>b</sup>	log K <sub>O<sub>2</sub></sub>	ΔH <sub>O<sub>2</sub></sub> <sup>b</sup>	TΔS <sub>O<sub>2</sub></sub> <sup>b</sup>
PYDIEN	14.73	-15.4	4.7	11.4	-32.6	-17.1
EPYDEN	13.99	-12.1	7.0	14.7	-34.2	-14.1
PYDPT	11.47	-13.1	2.5	7.7	-19.7	-9.2
IMDIEN	13.84	-13.2	5.7	12.6	-33.0	-15.8
IMDPT	11.36	-9.2	6.3	9.4	-20.1	-7.3

<sup>a</sup> Ligand abbreviations defined in ref 56. <sup>b</sup> Units of ΔH and TΔS = kcal/mol.

membered chelate rings with Co(II), and a lower stability linear correlation for pentamines that form two six-membered and two five-membered chelate rings. Therefore, it appears that something much different from the donor properties of the coordinated polyamine ligands influences the stabilities of these dioxygen complexes.

The search for an explanation of this unexpected and interesting behavior has led to X-ray crystallographic studies of coordinate bond distances<sup>61,62</sup> and to calorimetric studies of the thermodynamic parameters involved in the complexation and oxygen coordination reactions.<sup>63</sup> The bond distances and bond angles in the coordination sphere of [Co(PYDIEN)]<sub>2</sub>O<sub>2</sub>I<sub>4</sub><sup>62</sup> and of [Co(PYDPT)]<sub>2</sub>O<sub>2</sub>I<sub>4</sub>·3H<sub>2</sub>O<sup>61</sup> are indicated in the partial ORTEP drawings in Figure 4 (top and bottom, respectively), and the bond distances are listed together for comparison in Table III. It is seen that for the cobalt complexes containing two five-membered and two six-membered rings, the O-O distance is significantly shorter and the cobalt-oxygen distance is somewhat longer than for the complexes containing only five-membered chelate rings, thus indicating weaker dioxygen binding for ligands that form six-membered rings. Also, some of the nitrogen-cobalt distances are shorter (indicating stronger bonding) for the complexes containing only five-membered chelate rings. Thus we have the interesting situation whereby the six-membered chelate rings weaken the coordinate bonds between the basic nitrogen donor groups of the polyamine and the cobalt center, which in turn weaken the tendency of the metal ion to donate electrons to dioxygen to form the dioxygen complexes.

Calorimetric data<sup>63</sup> listed in Table IV show that the lower K<sub>O<sub>2</sub></sub> values of the dioxygen complexes containing two six-membered chelate rings involve much less favorable (less negative) enthalpy changes on oxygenation. On the other hand, the entropy changes that are generally very negative and unfavorable in dioxygen complex formation are considerably less negative for the

formation of the weaker complexes containing six-membered chelate rings. It is suggested that the entropy changes on dioxygen complex formation are due primarily to the following two factors. The negative entropy resulting from the loss of freedom of translation of the dioxygen molecule when it becomes complexed is common to all dioxygen complexes and probably does not vary much with the stability of the dioxygen complex that is formed. The second factor is the fact that on combination with dioxygen, the coordinate bonds of the metal become much stronger during the oxygenation process, thus tightening considerably the bonding of the polyamine ligand and greatly increasing the restriction of the internal partial rotations and vibrations of all the atoms in the ligand molecule. This entropy factor would be expected to become more negative (i.e., more unfavorable) as the strengths of the metal-nitrogen coordinate bonds increase.

The reciprocal relationship between the enthalpy and entropy of coordinate bonding is well-known. Thus any change that tends to strengthen the coordinate bonding of a ligand to a metal ion tends to restrict the motion of the donor atoms and the other adjacent atoms in the ligand molecule, resulting in a negative contribution to the entropy change on complexation. The entropy lost on dioxygen complex formation due to the tightening of the coordinate bonds as cobalt goes from cobalt(II) to cobalt(III) is greater for the complexes with the larger heats of dioxygen complexation and larger heats of increase in coordinate bond strength, as it should be. Data in Table III show that the N-Co bond distances in the two complexes are identical within experimental error for the highly basic aliphatic amino donor groups, but for the more weakly basic aromatic nitrogen donors, the coordinate bonds are significantly longer and weaker for the ligands containing two six-membered chelate rings. Detailed inspection of crystal structures<sup>61,62</sup> reveals considerably more distortion of bond angles and ring orientations in the PYDPT complex. Thus it appears that both ligands strive to maximize coordinate bond energies for the more basic aliphatic nitrogens, resulting in steric effects that strongly influence the energies of the coordinate bonds formed by the less basic nitrogens. Apparently, these steric factors are greater for the ligand containing the more highly folded six-membered chelate rings.

### Binucleating Ligands

Since stable dioxygen complexes of cobalt(II) in aqueous solution are generally binuclear, it was decided to study dioxygen complex formation from preformed binuclear cobalt(II) complexes. An interesting example of this type of complex is the binuclear cobalt(II) cryptate formed from BISTREN, the octamine cryptate ligand synthesized by Lehn and co-workers.<sup>64</sup>

(61) J. H. Timmons, A. Clearfield, A. E. Martell, and R. H. Niswander, *Inorg. Chem.*, **18**, 1042 (1979).

(62) J. H. Timmons, R. H. Niswander, A. Clearfield, and A. E. Martell, *Inorg. Chem.*, **18**, 2977 (1979).

(63) J. H. Timmons, A. E. Martell, W. R. Harris, and I. Murase, *Inorg. Chem.*, **21**, 1525 (1982).

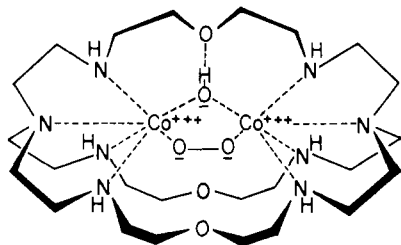
(64) J. M. Lehn, S. H. Pine, E. Watanabe, and A. K. Willard, *J. Am. Chem. Soc.*, **99**, 6766 (1977).

Table V  
Oxygenation and Stability Constants of Some  
Binuclear Co(II) Complexes

ligand <sup>a</sup>	equilibrium quotient	log equilibrium quotient ( $K_f$ , $K_{O_2}$ , $K'_{O_2}$ )
BISTREN, L	$\frac{[Co_2L^{4+}]}{[Co_2^{2+}][L]}$	16.35 ( $K_f$ )
	$\frac{[Co_2(OH)O_2L^{3+}]}{[Co_2L^{4+}]P_{O_2}}$	-5.45 ( $K'_{O_2}$ )
PXBDE, L	$\frac{[Co_2LL'_2^{4+}]}{[Co_2^{2+}]^2[L][L']^2}$	23.32 ( $K_f$ )
EN, L'	$\frac{[Co_2LL'_2O_2^{4+}]}{[Co_2L^{4+}]^2}$	6.71 ( $K_{O_2}$ )
BISDIEN	$\frac{[Co_2L^{4+}]}{[Co_2^{2+}]^2[L]}$	12.4 ( $K_f$ )
	$\frac{[Co_2O_2(OH)L^{3+}][H^+]}{[Co_2L^{4+}]P_{O_2}}$	-3.29 ( $K'_{O_2}$ )
	$\frac{[Co_2L^{4+}]P_{O_2}}{[Co_2^{2+}]^2[L]}$	

<sup>a</sup> Ligand abbreviations defined in ref 56.

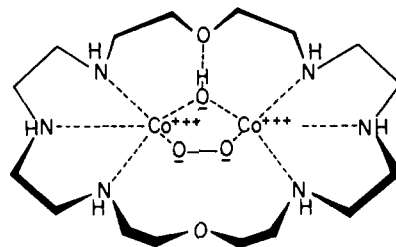
This ligand is designed to coordinate two metal ions within the crypt with sufficient distance between them to coordinate bridging ligands containing two or three atoms. A conceptual illustration of how this cryptand ligand may coordinate two cobalt ions with a dioxygen bridge between them is indicated by formula 2. Since



2, dicobalt dioxygen complex of BISTREN

each metal ion is coordinated to only four nitrogen donors, the dioxygen complex would be expected to also have a hydroxo bridge, an expectation which has been borne out by potentiometric equilibrium studies.<sup>65</sup> The formation constant of the dicobalt BISTREN dioxygen complex (Table V) is much lower than would have been predicted on the basis of the basicities of the ligand donor groups. There are several possible reasons for this behavior. The most probable reason is a poor fit for the peroxo and hydroxo bridges in the dicobalt cryptate complex. One of the difficulties encountered in the bistren complexes is the long time required for reaching equilibrium. Slow kinetics is apparently the result of the considerable time it takes for reacting molecules and ions to enter and leave the cage-like structure of the cryptand ligand.

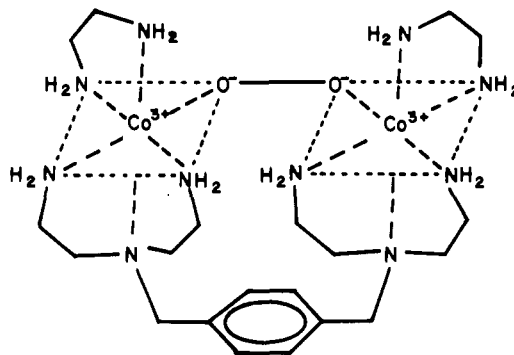
An analogous macrocyclic binucleating ligand, BISDIEN (3), has two diethylenetriamine ligands in a relatively flexible ring structure but with the same bridging groups as those of BISTREN.<sup>64</sup> This ligand also forms a binuclear cobalt dioxygen complex with hydroxo and peroxo bridges between the metal ions. The formation constants for the oxygenation of the dicobalt BISTREN<sup>65</sup> and BISDIEN<sup>66</sup> complexes, listed



3, dicobalt dioxygen complex of BISDIEN

in Table V, indicate that the cobalt(II) complex of the more flexible ligand BISDIEN forms a much more stable dioxygen complex in spite of its lower basicity and smaller number of basic donor groups. These facts reinforce the interpretation that steric factors reduce the stability of the cobalt bistren dioxygen complex.

The oxygen complex of a more open type binucleating ligand, pxbde, having two diethylenetriamine coordinating moieties undergoes more rapid oxygenation kinetics than do its cyclic analogues 2 and 3. This ligand forms a binuclear cobalt complex in which the metal ions are sufficiently far apart to combine simultaneously with dioxygen in the presence of an added bidentate ligand, such as ethylenediamine, to form dioxygen complexes of the type indicated by 4. Each metal ion



4, dioxygen complex formed from ethylenediamine and PXBDE

is pentacoordinated by basic nitrogen donor groups so that the addition of dioxygen completes the six-coordination requirement of the cobalt(III) centers. Equilibrium constants<sup>67,68</sup> for dioxygen complex formation from the Co(II) complex of PXBDE are presented in Table V.

### Stabilities of Various Types of Dioxygen Complexes

An overview of the types of equilibrium data available on dioxygen complex formation is provided in Table VI. For comparison of complexes measured under differing conditions, the oxygenation constants are given as the reciprocal of the equilibrium oxygen pressure for systems in which a metal complex is half converted to the corresponding dioxygen species. These formation constants are concentration independent except for the formation of binuclear cobalt dioxygen complexes in solution from mononuclear complexes (no. 6-8 in Table VI). For such complexes  $1.0 \times 10^{-3}$  M solutions are taken as the reference state.

(65) R. J. Motekaitis, A. E. Martell, J. M. Lehn, and E. Watanabe, *Inorg. Chem.*, in press.

(66) R. J. Motekaitis, A. E. Martell, E. Watanabe, and J. M. Lehn, submitted for publication.

(67) C. Y. Ng, A. E. Martell, and R. J. Motekaitis, *J. Coord. Chem.*, 9, 255 (1979).

(68) C. Y. Ng, R. J. Motekaitis, and A. E. Martell, *Inorg. Chem.*, 18, 2982 (1979).



Table VI  
Comparison of Stabilities of Various Types of Dioxygen Complexes<sup>a</sup>

no.	O <sub>2</sub> -free complex	dioxygen complex	$P_{1/2}^{-1}$ (atm <sup>-1</sup> )	conditions
1	human hemoglobin A, Hb	Hb·O <sub>2</sub>	$4.0 \times 10^2$	25 °C, pH 7.4 (Tris buffer)
2	FeTPivPP (Me <sub>2</sub> Im), MLL'	MLL'O <sub>2</sub>	$2.0 \times 10^1$	25 °C, toluene
3	CoTPivPP (Me <sub>2</sub> Im), MLL'	MLL'O <sub>2</sub>	$8.4 \times 10^{-1}$	25 °C, toluene
4	Co(SALEN), ML	(ML) <sub>2</sub> O <sub>2</sub>	2.3	20 °C, Me <sub>2</sub> SO
5	Co(ACACEN)PY, MLL'	MLL'O <sub>2</sub>	$4.0 \times 10^2$	-31 °C, toluene
6	Co(TEP) <sup>2+</sup> , ML	(ML) <sub>2</sub> O <sub>2</sub>	$3.4 \times 10^{13}$	25 °C, $\mu = 0.10$
7	Co(TREN) <sup>2+</sup> , ML	(ML) <sub>2</sub> (O <sub>2</sub> )(OH)	$1.4 \times 10^9$	25 °C, $\mu = 0.10$ , pH 7
8	Co(BPY)(TERPY) <sup>2+</sup> , MLL'	(MLL')O <sub>2</sub>	$1.4 \times 10^3$	25 °C, $\mu = 0.10$
9	Co <sub>2</sub> (BISTREN)OH <sup>3+</sup> , M <sub>2</sub> LL'	(M <sub>2</sub> LL')O <sub>2</sub>	$3.5 \times 10^1$	25 °C, $\mu = 0.10$ , pH 7
10	Co <sub>2</sub> PXBDE(EN) <sub>2</sub> <sup>4+</sup> , M <sub>2</sub> LL <sub>2</sub> '	(M <sub>2</sub> LL <sub>2</sub> ')O <sub>2</sub>	$5.1 \times 10^6$	25 °C, $\mu = 0.10$
11	Co <sub>2</sub> BISDIEN <sup>4+</sup> , M <sub>2</sub> L	(M <sub>2</sub> L)(O <sub>2</sub> )(OH)	$5.1 \times 10^4$	25 °C, $\mu = 0.10$ , pH 7

<sup>a</sup> Ligand abbreviations defined in ref 56.

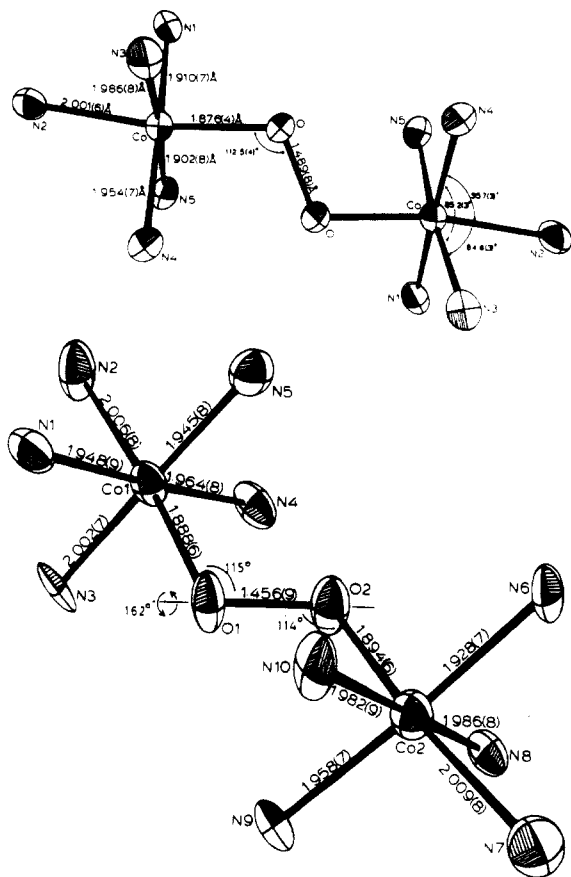


Figure 4. Partial ORTEP drawings of portions of the coordination spheres of dioxygen complexes showing bond angles and distances of atoms bonded to the metal ion: top, [Co(PYDIEN)]<sub>2</sub>O<sub>2</sub>I<sub>4</sub>; bottom, [Co(PYDPT)]<sub>2</sub>O<sub>2</sub>I<sub>4</sub>·3H<sub>2</sub>O.

The oxygenation constant listed for hemoglobin, which involves an equilibrium pressure of about 2 torr, was measured *in vitro* and is higher than the stability constant of hemoglobin under physiological conditions. The equilibrium pressure for the "picket-fence" iron dioxygen complex (no. 2) seems to be much closer to

the working pressure of hemoglobin in living systems. It is noted that the equilibrium constant for the corresponding cobalt dioxygen complex is approximately 20 times smaller than that of iron under comparable reaction conditions. Although the synthetic oxygen carriers containing porphyrin or Schiff base ligands (formulas 2–5) have stabilities within a reasonable range of those of natural oxygen carriers, their lack of solubility in water and the low temperatures required for the acetylacetonate Schiff base complex offer serious difficulties for the investigation of reaction kinetics and mechanisms involving these complexes. The dioxygen affinities of cobalt complexes containing highly basic ligands such as TEP and TREN are much too high for comparison with natural oxygen carriers because the equilibrium pressure of oxygen in such systems would be extremely low and perhaps unmeasurable. These complexes would release oxygen, however, in solutions that are sufficiently acidic to induce partial protonation and dissociation of the polyamine donor ligands. As mentioned above, the low stability of the cobalt BISTREN dioxygen complex may be due to steric effects rather than to the coordinating properties of the ligand, which would otherwise be expected to promote the formation of a complex of very high stability. This view seems to be borne out by the higher stability of the dioxygen complex 11 of BISDIEN, a relatively flexible macrocyclic base which has two less basic amino groups than does BISTREN. Although compounds 6–11 are not good models for hemoglobin or other dioxygen carriers, they may be used as models for oxidase and oxygenase enzymes. These complexes and other cobalt dioxygen complexes described above provide interesting opportunities for studying the reactivities of oxygen complexes as oxidants and could provide insights into how reactivities of dioxygen complexes vary with the strength of metal–dioxygen bonding.

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