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Hydroxo-bridged dinuclear cobalt(II) complexes of OBISDIEN and OBISTREN as oxygen carriers

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The hydroxo-bridged dinuclear cobalt(II) complexes of the macrocyclic and macrobicyclic dinucleating ligands OBISDIEN and OBISTREN form thermodynamically stable dioxygen adducts. Although the values of the oxygenation constants of cobalt complexes usually increase with an increase in the number of basic amino groups coordinated to the cobalt centers, these complexes are unusual in that the oxygenation constants of the complex formed from OBISDIEN is about three orders of magnitude higher than the analogous complex formed from OBISTREN. The difference in behavior must be due to differences in steric strain. Since crystal structures are not available, steric effects were estimated by the use of molecular mechanics. By application of the molecular modelling program SYBYL it was determined that the distortions of the cryptand ligand necessary to form the hydroxo-bridged dioxygen complex are much greater and more energetic than those of the macrocyclic ligand. Both ligands were found to form excellent oxygen carriers because of facile oxygenation-deoxygenation reactions of their dinuclear cobalt complexes, and because of almost immeasurably slow metal-centered degradation. Moreover, the ligands were not changed during degradation, so that the oxygen-carrying complexes could be easily regenerated by electrolytic reduction.

INTRODUCTION

The chemical separation of dioxygen from dinitrogen and other gases present in air has been considered a potentially effective method, capable of commercial application, because of 100% selectivity in the formation of dioxygen adducts of certain transition metal complexes. The dioxygen adducts of cobalt(II) complexes have received the most attention, since cobalt(II) complexes have shown the most versatility in combining with dioxygen to form complexes having a range of stability from very low to very high. Thus the equilibrium with dioxygen in aqueous solution, or between oxygen gas and the solid dioxygen complex, can be used to form the dioxygen complex from a mixture of gases, with free dioxygen pressures or concentrations that are indicated by the oxygenation equilibrium constant. The formation of dioxygen complexes is always exothermic, with a very unfavorable entropy change (very negative). The dioxygen complexes formed can be made to dissociate and release pure dioxygen by increasing the temperature, lowering the pressure, or both. When the dioxygen adduct is formed in aqueous solution from the metal complex of a basic ligand, the stability of the complex can be reduced, and the oxygen released, by lowering the pH.

The main property of dioxygen complexes that has prevented their application to dioxygen separation processes is the activation of the dioxygen by complexation, thus promoting its attack on the ligand which coordinates the cobalt(II) ion (or other transition metal ion). This oxidative attack on the ligand, whether it be initially oxygen insertion or dehydrogenation, results in a reduction of the coordinating ability of the ligand and eventually to the destruction of the metal complex which initially combines with dioxygen. In some cases the degradation is metal-centered oxidation in which the metal is oxidized to its higher valence state, the oxygen is released as hydrogen peroxide (in water or a protic solvent), and the ligand is in general unchanged. All dioxygen complexes undergo degradation, some very rapidly and others more slowly, with half-lives of days or more. It is the degradation reaction which must be overcome, or effectively slowed to the extent that it is negligible, before a metal complex can be developed commercially as a chemical reagent for dioxygen separation from air.

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The formation and degradation of cobalt(II) dioxygen complexes can be represented by the following chemical equations:

Formation:

$LCo^{2+} + O_2 \rightleftharpoons LCo^{3+}\text{-}O^{-}\text{-}O^{\cdot}$ 1:1 complex; cobalt superoxide

$LCo^{3+}\text{-}O^{-}\text{-}O^{\cdot} + Co^{2+} \rightleftharpoons L\ LCo^{3+}\text{-}O^{-}\text{-}O^{-}\text{-}Co^{3+}L$

1:2 complex; peroxo bridged binuclear cobalt complex

Degradation

$LCo^{3+}\text{-}O^{-}\text{-}O^{-}\text{-}Co^{3+}L + 2H^{+} \longrightarrow 2Co^{3+}L + H_2O_2$

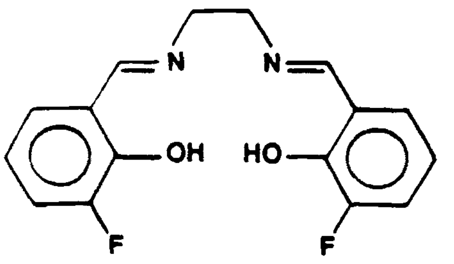
Metal-centeredoxidation

$LCo^{3+}\text{-}O^{-}\text{-}O^{-}\text{-}Co^{3+}L \longrightarrow 2Co^{2+}H_{-2}L + 2H_2O$

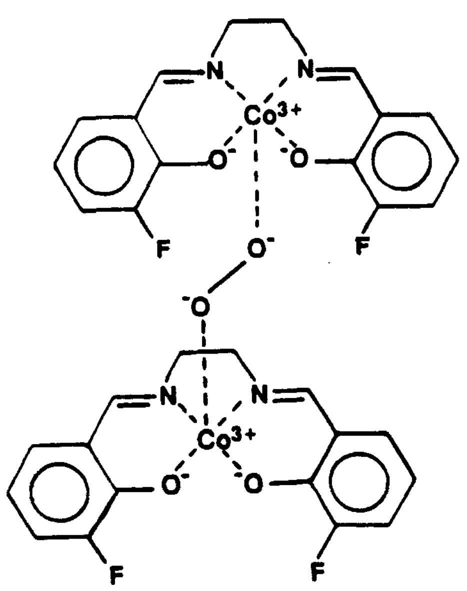
Ligand-centered oxidation such as Schiff base formation

In the above equations the charge of the ligand L is assumed to be zero for simplicity, but can vary considerably. When metal-centered oxidation takes place the dioxygen complex may be regenerated by reducing the metal ion, since the ligand is not affected by the degradation reaction. Only one kind of ligand-centered oxidation (degradation) is shown. Schiff base formation requires the removal of two hydrogen atoms and generation of a double bond, usually conjugated with an aromatic ring. There are many other types of ligand oxidation reactions that are possible, such as oxygen insertion to change a -CH- group to -C-OH- (hydroxylation) or dehydrogenation of an alcohol to an aldehyde. Eventually, the ligand can be completely destroyed by the activated dioxygen.

The first metal chelate to be developed for the separation of dioxygen is the cobalt(II)-Schiff base complex formed from 3-fluorosalicylaldehyde and ethylenediamine. The ligand, named "fluomine" indicated by formula **1**, has been described in detail by Martell and Calvin.[1] Its dioxygen complex, **2**, in the solid state undergoes a facile exchange of dioxygen with air, because dioxygen rapidly diffuses through the crystalline carrier. This compound was developed for the U.S. Air Force for the preparation of pure dioxygen from air.[2,3] Under practical conditions, with moderately large scale equipment, about 5,000 cycles of oxygenation and deoxygenation were achieved over a 7-10 month period during which the carrier was degraded to about 50% of its effectiveness. This was considered adequate for special purposes, such as the production of oxygen for aircraft personnel, but was not considered competitive with large-scale industrial (cryoscopic) production of oxygen from air.



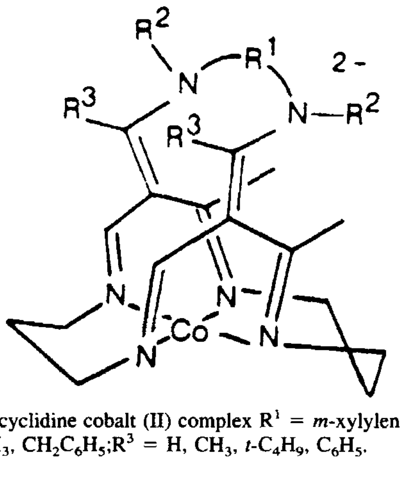
1 Bis(3-fluorosalicylaldehyde)ethylene-diimine (Fluomine).



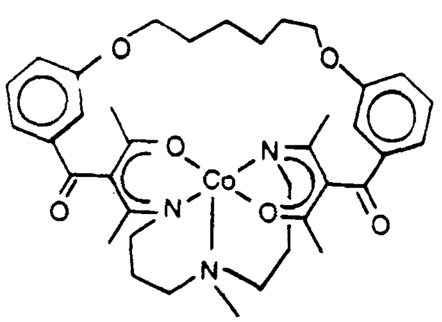
2 Binuclear cobalt dioxygen complex of fluomine.

Another area of dioxygen complex chemistry applied to the separation of dioxygen from air is cobalt lacunar cyclidine Schiff base complexes (dry caves) synthesized by Busch and coworkers.[4] Examples are illustrated by formulas **3** and **4**.

These complexes were generally used in acetonitrile or toluene solvents, and coordinate dioxygen as 1:1 complexes (superoxides) in a protected pocket inaccessible to molecules of large or moderate size. Four-coordinate complexes represented by **3** require an axial base (usually N-methylimidazole or pyridine) for dioxygen complexation, while **4** and its analogs have the axial basic donor group built in, producing a 5-coordinate cobalt(II) complex directly without an added base. The structures



3 Lacunar cyclidine cobalt (II) complex R^1 = *m*-xylylene, $(CH_2)_{4\text{-}8}$; R^2 = H, CH_3, $CH_2C_6H_5$;R^3 = H, CH_3, *t*-C_4H_9, C_6H_5.



4 A lacunar Co(II) Schiff base complex.

of these complexes were varied considerably, producing dioxygen complexes having wide variations of thermodynamic stability. Although 1:1 dioxygen complex formation was considered an advantage in dioxygen separation and transport, the rates of degradation of the dioxygen complexes were disappointingly large, with half lives varying from a few hours to a few days.

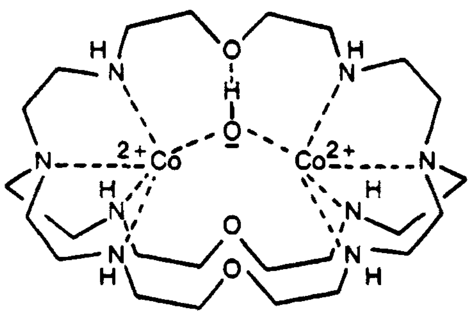
Others have described the use of special apparatus to obtain the separation of oxygen from air. For example Roman[5] described an oxygen-permeable membrane to separate the air stream from the dioxygen complex solution. The feed stream was kept at a sufficiently high pressure to facilitate the diffusion of the oxygen from the mixture through the membrane to form the complex. The product stream, consisting of pure dioxygen, was kept at a pressure low enough to convert the carrier to its deoxygenated form, so that the purified dioxygen would diffuse into it through the membrane. The temperature was also varied, with a lower temperature in the feed stream to facilitate formation of the dioxygen complex and a higher temperature in the product stream favoring its dissociation. Achieving concentrations of dioxygen of 95-99% and a service life of the carrier of about three months were claimed for the method.

Zenner et al.[6] disclosed the electrolytic method, whereby the dioxygen was released by the carrier at the anode to the product stream, with the formation of the Co(III) complex. The carrier (Co(II) complex) would be generated at the cathode, where it would come in contact with the feed stream (air) and regenerate the dioxygen complex. Cobalt polyamines that form peroxo-bridged dioxygen complexes, were usually used as carriers. A typical cycle would be:

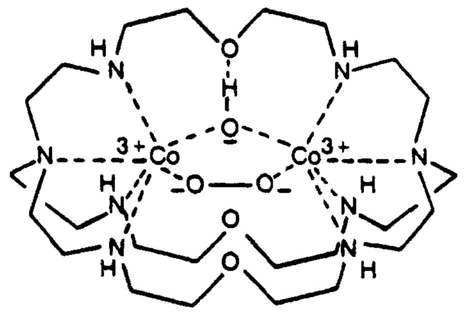
$$\text{Anode reaction: } (\mathrm{LCo})_2\mathrm{O}_2^{4+} \longrightarrow 2(\mathrm{LCo}^{3+}) + \mathrm{O}_2 + 2\mathrm{e}^-$$

$$\text{Cathode reaction: } 2\mathrm{LCo}^{3+} + \mathrm{O}_2 + 2\mathrm{e}^- \longrightarrow (\mathrm{LCo})_2\mathrm{O}_2^{4+}$$

Although the electrolytic process is very attractive in principle, various problems developed when it was brought up to a pilot plant scale, which cut down the efficiency of the process.



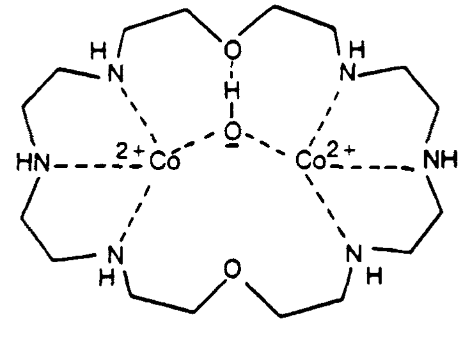
5 μ-hydroxo-dicobalt OBISTREN cryptate.



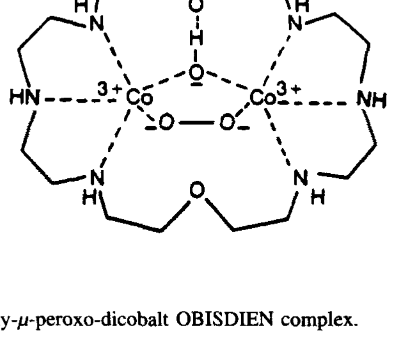
6 μ-hydroxy-μ-peroxo-dicobalt OBISTREN cryptate.

Oxygen Adducts of Dinculear Cobalt OBISTREN and OBISDIEN Complexes

The formulas of the hydroxo-bridged dinuclear cobalt (II)-BISTREN complex, an oxygen carrier, and the dioxygen complex that it forms, are indicated by **5** and **6**.[7]



7 μ-hydroxo-dicobalt OBISDIEN complex.



8 μ-hydroxy-μ-peroxo-dicobalt OBISDIEN complex.

Table 1 Comparison of stabilities of dicobalt dioxygen complexes formed from OBISTREN and OBISDIEN

Carrier	*Dioxygen complex*	*Log* $K_{O_2}^{a}$	$P_{1/2}^{-1}$ *(atm^{-1})*	*Conditions*
$Co_2(OH)$OBISTREN, **5**	$Co_2(OH)O_2$OBISTREN, **6**	-6.00	3.5×10^1	25.0°C, $\mu = 0.10$ M p[H] = 7.0
$Co_2(OH)$OBISDIEN, **7**	$Co_2(OH)$OBISDIEN, **8**	-3.29	5.1×10^4	25.0°C, $\mu = 0.10$ M p[H] = 7.0

[a] $K_{O_2} = [Co_2(OH)O_2L^{3+}][H^+]/[Co_2L^{4+}]P_{O_2}$ M atm^{-1}, where L = OBISTREN or OBISDIEN.

OBISDIEN is a binucleating macrocyclic ligand which forms a dinuclear cobalt(II) complex, **7**,[8] which in turn forms a cobalt dioxygen complex, **8**, very similar to the dioxygen complex 6, formed from cobalt(II) and OBISTREN. The dioxygen complex formed from OBISTREN involves four basic nitrogen donors per metal ion and should have a much higher oxygenation constant than the dioxygen complex formed from dicobalt OBISDIEN, in which there are three basic nitrogen donors per metal ion. The fact that the latter is over three orders of magnitude more stable (Table 1) indicates that the dioxygen complex formed from the dicobalt(II) OBISTREN cryptate complex has unexpectedly low thermodynamic stability, probably because of the less flexible nature of the cage (i.e. for steric reasons).

Comparison of Formation of Dioxygen Complexes from Cobalt(II) Dinuclear Complexes of OBISTREN and OBISDIEN with Complexes formed from Other Macrocyclic and Cryptand Ligands

Both Co_2L complexes absorb oxygen rapidly at 25.0°C from air at about pH 9 (Figs. 1 and 2). As expected, $Co(II)_2$-OBISDIEN, a macrocyclic complex, absorbs oxygen more quickly than $Co(II)_2$-OBISTREN, a cryptate complex. The $Co(II)_2$-OBISTREN can reversibly absorb dioxygen from air at room temperature and can undergo many oxygenation and deoxygenation cycles without any appreciable loss of the dinuclear complex. Other macrobicyclic ligands in Table 2[9,10] either do not absorb dioxygen (tris(furan)BISTREN and tris-(*p*-xylyl)BISTREN) or their dioxygen complexes undergo rapid irreversible degradation. Therefore the hydroxo-bridged dicobalt OBISTREN cryptate, **5**, is unique among the dinuclear dicobalt cryptate complexes in Table 2 in its almost immeasurably slow rate of degradation.

Macrocyclic Ligands

Among the seven macrocyclic ligands identified below, the $Co(II)_2$-OBISDIEN forms the most stable dioxygen complex with respect to degradation. For the other six ligands (Table 3), the cobalt(II) dioxygen complexes undergo irreversible degradation at room temperature.[9,10] Some complexes absorb oxygen rapidly such as $Co(II)_2$-C4BISDIEN ($t_{1/2} = 4.0$ min, which is nearly the same as the $t_{1/2} = 4.5$ min of $Co(II)_2$-OBISDIEN) but its dioxygen complex only exists for several hours.

Rates of Degradation of the Oxygen Complexes Obtained from OBISTREN and OBISDIEN

Recently Motekaitis and Martell[11,12] described the formation, dissociation, and degradation of the binuclear cobalt OBISTREN dioxygen complex, and suggested its use as an oxygen carrier for oxygen separation from air. The rate of degradation of this dioxygen complex was

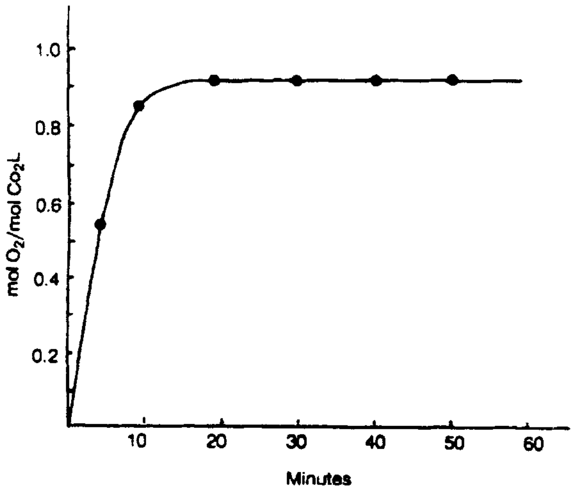


Figure 1 Dioxygen absorption by the $Co(II)_2$-OBISDIEN complex (1.2×10^{-3} M) at 15 °C, $P_{O_2} = 151$ mm Hg and pH = 8.5; mole O_2/mole Co_2L *vs* minutes; $t_{1/2} = 4.5$ min.

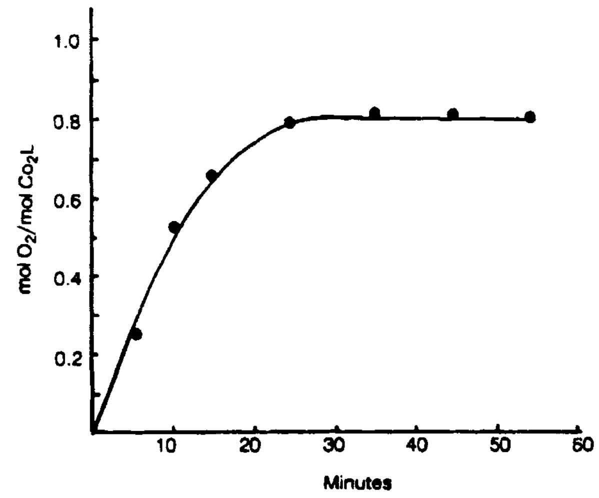
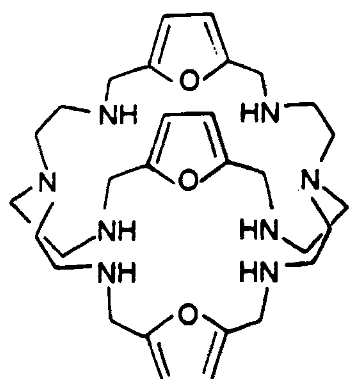
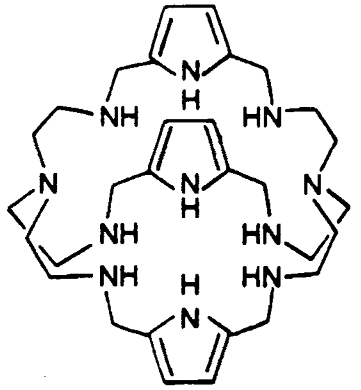


Figure 2 Dioxygen absorption by the $Co(II)_2$-OBISTREN complex (1.2×10^{-3} M) at 15 °C, $P_{O_2} = 152$ mm Hg and pH = 8.4; mole O_2/mole Co_2L *vs* minutes; $t_{1/2} = 10$ min.

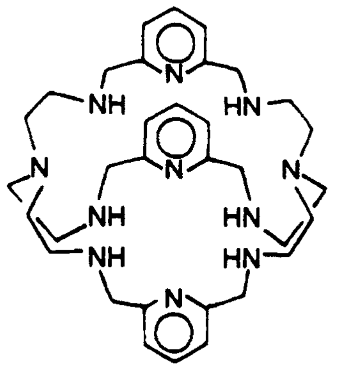
Table 2 Macrobicyclic ligands and the time of 50% oxygenation for their dinuclear cobalt(II) complexes and approximate rates of degradation of the dioxygen complexes



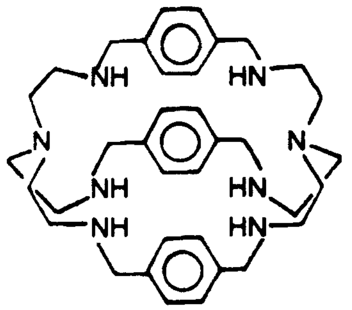
9 Tris(furan)BISTREN



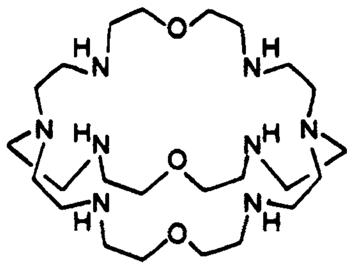
10 Tris(pyrrole)BISTREN
$t_{1/2}$ = 60 min (formation)
$t_{1/2}$ ≃ 3 hr (decay)



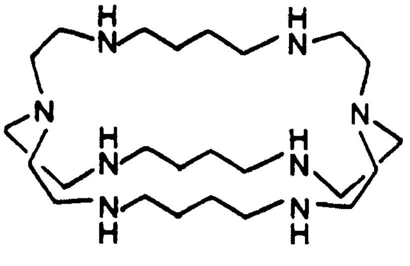
11 Tris(pyridine)BISTREN
$t_{1/2}$ = 34 min (formation)
$t_{1/2}$ ≃ 3 hr (decay)



12 Tris-(*p*-xylyl)BISTREN



13 OBISTREN
$t_{1/2}$ = 10 min (formation)
$t_{1/2}$ ≃ 3 mo (decay)



14 C4BISTREN
$t_{1/2}$ = 12.5 hr (formation)
$t_{1/2}$ ≃ several days (decay)

too slow to be measured at room temperature and moderately elevated temperature, but at 95°C the first order rate constant for its degradation was reported as 3.7×10^{-5} s^{-1}. On this basis the estimated degradation rate at 55°C is about 1×10^{-6} s^{-1}, and at 25°C, 1×10^{-7} s^{-1}. The degradation is metal-centered, so that the ligand is not affected by the redox reaction that occurs on degradation. The reaction sequence is:

$$\text{Oxygenation: } \mathrm{Co_2(OH)OBISTREN^{3+}} + \mathrm{O_2} \xrightleftharpoons{\text{fast}} \mathrm{Co_2(OH)O_2OBISTREN^{3+}}$$

$$\text{Degradation: } \mathrm{Co_2(OH)O_2OBISTREN^{3+}} + 2\mathrm{H^+} \xrightarrow{\text{slow}} \mathrm{Co_2(OH)OBISTREN^{5+}} + \mathrm{H_2O_2}$$

$$\text{Disproportionation: } \mathrm{H_2O_2} \longrightarrow \mathrm{H_2O} + 1/2\,\mathrm{O_2}$$

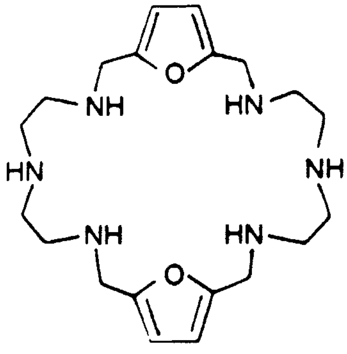
Figure 3 shows that after standing at room temperature for one month the peak (about 370 nm) for the Co(II)$_2$-OBISDIEN dioxygen complex only decreases slightly. If one assumes that the dioxygen complex of Co(II)-OBISDIEN degrades by about 25% in thirty days (as indicated by Figure 3), the first order rate constant for its degradation comes out as about 1×10^{-7} sec^{-1}, surprisingly close to the value estimated for the degradation of the dioxygen complex of Co(II)$_2$-OBISTREN

The fact that both Co(II)$_2$-OBISTREN and Co(II)$_2$-OBISDIEN form tremendously stable (against degradation) dioxygen complexes compared with other complexes is possibly due to the flexible ether oxygens as bridging groups, which the other ligands do not have. Although the bis(furan)BISDIEN contains an oxygen bridge, it is not an ether oxygen, is part of a rigid aromatic structure, and is not flexible. It seems that the flexible ether oxygen plays a very important role in stabilizing the dioxygen complex.

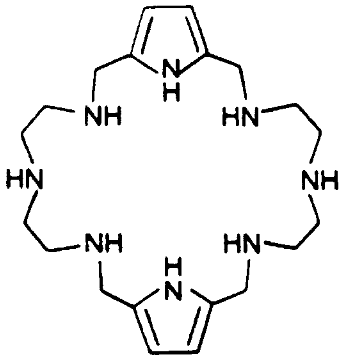
Probable Structures of the Dicobalt Dioxygen Complexes

In Figure 4 are shown the molecular mechanics generated structures of [(CoEN$_2$)$_2$-μ-O$_2$-μ-OH] (referred to here as the bis-EN complex), [Co$_2$(OBISDIEN)(H$_2$O)$_2$-

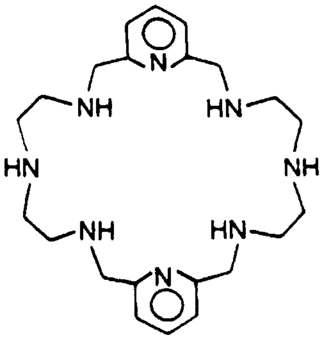
Table 3 Macrocyclic ligands and the time of 50% oxygenation for their Co(II) complexes and approximate rates of degradation of the dioxygen complexes



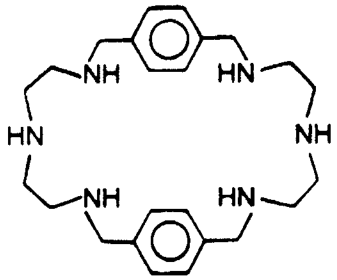
15 Bis(furan)BISDIEN
$t_{1/2}$ = 40 min (formation)
$t_{1/2} \simeq$ 3 hr (decay)



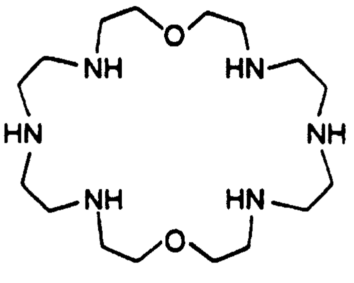
16 Bis(pyrrole)BISDIEN
$t_{1/2}$ = 24 min (formation)
$t_{1/2} \simeq$ 3 hr (decay)



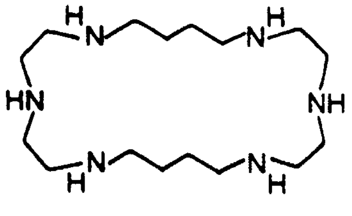
17 Bis(pyridine)BISDIEN
$t_{1/2}$ = 34 min (formation)
$t_{1/2} \simeq$ 3 hr (decay)



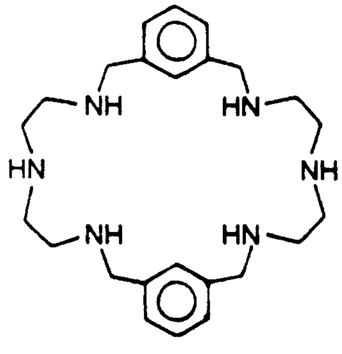
18 Bis-(*p*-xylyl)BISDIEN
$t_{1/2}$ = 20 min (formation)
$t_{1/2} \simeq$ 3 hr (decay)



19 OBISDIEN
$t_{1/2}$ = 4.5 min (formation)
$t_{1/2} \simeq$ 3 mo (decay)



20 C4BISDIEN
$t_{1/2}$ = 4.0 min (formation)
$t_{1/2} \simeq$ several min (decay)



21 BisMXBISDIEN
$t_{1/2}$ = 20 min (formation)
$t_{1/2} \simeq$ several min (decay)

μ-O_2-μ-OH] (the OBISDIEN complex) and [Co_2OBISTREN-μ-O_2-μ-OH] (the OBISTREN complex).[13] The important characteristic of the OBISTREN complex is that all the structural features are to be understood in terms of the Co to Co distance being quite long to accommodate both the peroxo and hydroxo bridging groups. Therefore the bridging peroxo and hydroxo groups are coordinated to the metal centers with considerable steric strain. This is reflected in the steady increase in the Co-Co distance from 3.29 Å in the nearly strain-free bis-EN complex to 3.45 Å in the OBISTREN complex. a result of this, one sees features in the OBISTREN structure such as the Co-O-CO nd angle being progressively opened out from 118.8° in the

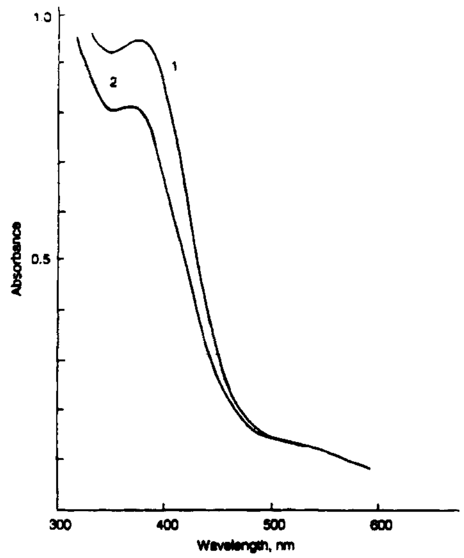


Figure 3 Uv-visible absorbance spectra of dioxygen complex of Co(II)$_2$-OBISDIEN (2.4 × 10^{-3} M) measured at 25 °C and pH 8.5. 1, Dioxygen complex; 2, Measured after standing at 25 °C for 30 days.

bis-EN complex to 125.7° ???? OBISTREN complex. The Co-O-O-C torsion angle is flattened from 54.6° in the bis-EN 45.0° in the OBISTREN complex. The Co-O bond length for the bond to the ???? group is stretched from 1.86 Å in the bis-EN complex to 1.90 Å in the OBISTREN complex. The Co-N bonds in the OBISTREN complex are all considerably longer than the comparable bonds in the bis-EN complex. Thus, the Co-N bonds cis to both oxygens coordinated to the cobalt are 2.03 Å, which is at the extreme limit of Co-N bond lengths, as seen in Figure 4. One concludes that the reversibility of O_2 loading by the OBISTREN complex relates simply to the strain produced by coordination of a peroxo group. In contrast, the geometry around Co(III) in the OBISDIEN complex is not greatly distorted, and all of the Co-N distances fall within the normal range, of about 1.95–1.98 Å, seen in simple amine complexes of Co(III). One concludes therefore that the much stronger binding of oxygen by the OBISDIEN complex relates to

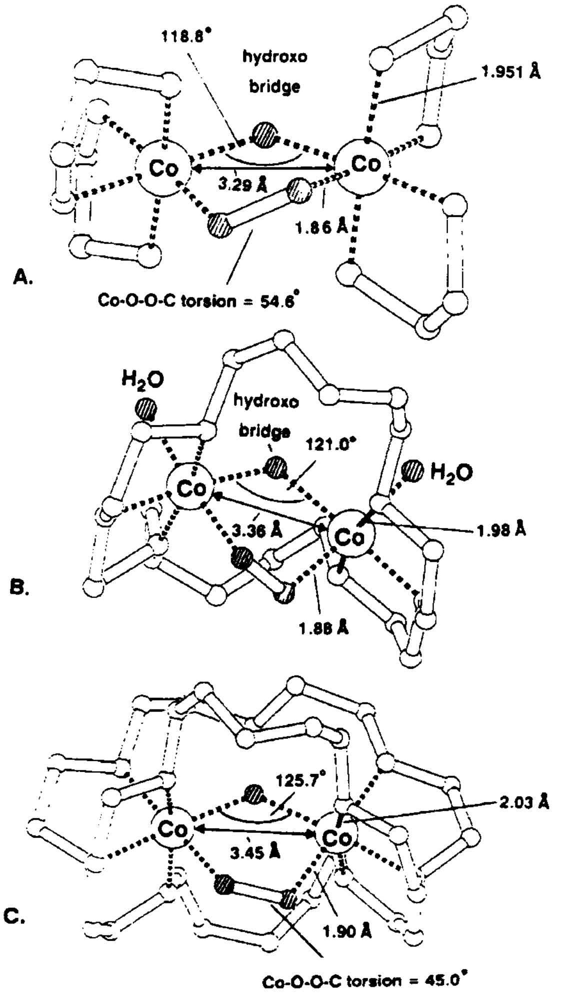
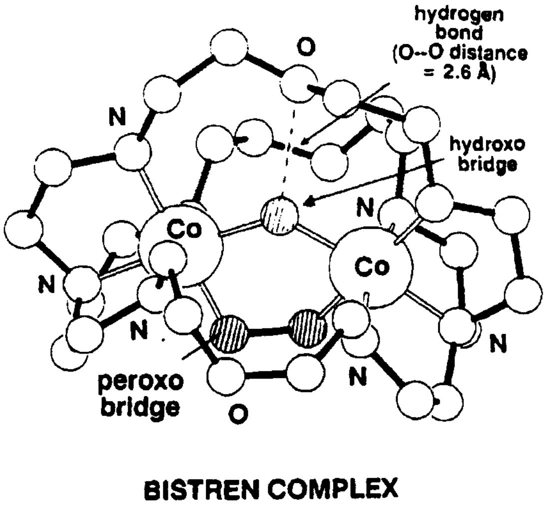
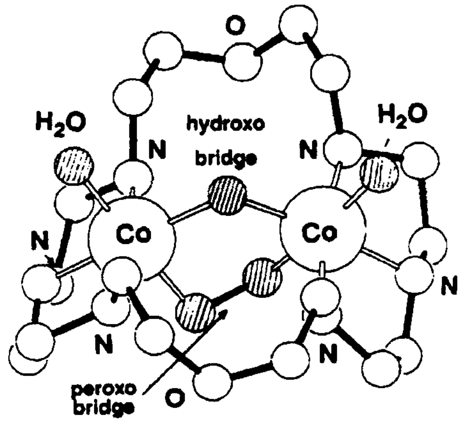


Figure 4 Molecular mechanics simulation of the structures of the dioxygen complexes formed from the dicobalt(II) complexes of OBISDIEN and OBISTREN and the bis(ethylenediamine)cobalt(II) complex.



BISTREN COMPLEX



BISDIEN COMPLEX

Figure 5 A view of the simulated structures of dioxygen complexes formed from the dicobalt(II) complexes of OBISDIEN and OBISTREN, showing a hydrogen bond formed in the OBISTREN complex and the lack of a hydrogen bond in the OBISDIEN complex.

considerably lower steric strain in the coordination sphere of the two cobalt(III) ions.

A somewhat different view of the dioxygen complexes derived from OBISDIEN and OBISTREN is shown in Figure 5. In the OBISTREN cobalt dioxygen complex the bridging hydroxo group is close enough to one of the ether oxygens to form a hydrogen bond. On the other hand, the ether oxygens in the lowest strain structure of the dioxygen complex derived from dicobalt OBISDIEN are too far from the bridging hydroxo group to form a hydrogen bond.

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