

# Thermodynamics of coordination of metal ions with binucleating macrocyclic and macrobicyclic ligands

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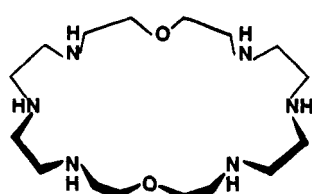
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**Abstract.** The stabilities of the Cu(II) complexes of binucleating macrocyclic and macrobicyclic ligands, and the equilibrium constants with bridging anions for the Cu(II) and Co(II) complexes formed by these ligands, are described. The binuclear Co(II) dioxygen complexes are presented as examples of a bridging anion coordinated simultaneously to two metal centers.

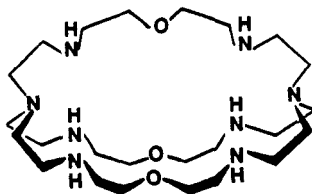
## INTRODUCTION

This paper describes thermodynamic measurements of the affinities of binucleating macrocyclic and macrobicyclic ligands with transition metal ions and the ability of the binuclear complexes thus formed to "recognize" and combine with various anions as bridging groups (ref. 1,2,3). Thermodynamic measurements provide no information about the structure of the complexes formed. The nature of the coordination sites depends on comparison with other ligands, and on microscopic information such as absorption spectra and NMR spectra which indicate the coordination sites that are altered on complex formation. Also valuable information on structure of the complex formed can be obtained from X-ray crystal structure data, keeping in mind that the coordination sites in the solid state may be quite different from those in solution. However, many metal complexes retain their specific donor sites and coordination geometry whether they are in solution or in the solid state. Thermodynamic values of free energies of complex formation (or stability constants), enthalpies and entropies of complex formation will be used in this paper in conjunction with any additional information that is available on the nature of the coordination sites. Also structural data will be used where possible as a help in determining the nature of the complexes formed.

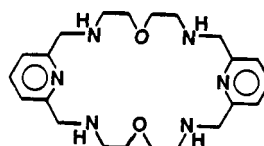
The parent ligands described in this paper are O-BISDIEN, **1**, and O-BISTREN, **2**. In addition, the related ligands O1-BISBAMP, **3**, which has two pyridine rings fused into the BISDIEN structure, O2-BISBAMP, **4**, which has double ether bridges in place of single ether oxygens in the bridging groups between the bisaminopyridyl moieties of O1-BISBAMP, and C-BISTREN, **5**, which has carbon atoms in place of ether oxygens in the bridging groups between the TREN moieties of O-BISTREN, are also described.



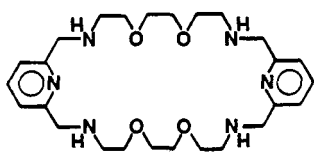
1 O-BISDIEN



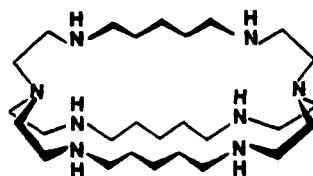
2 O-BISTREN



3 O1-BISBAMP



4 O2-BISBAMP



5 C-BISTREN

The affinities of these ligands for the transition metal ions is greatest for **2** and **5** which have four basic amino groups on each end of the molecule. The three secondary nitrogens in the O-BISTREN moiety are quite basic while the central tertiary nitrogen has a much lower basicity due to repulsion of protons by the  $\text{NH}_2^+$  groups. Formula 1 shows a macrocyclic ligand usually called O-BISDIEN in which two diethylenetriamine moieties are separated by ethylether bridges. This ligand has less affinity for metal ions than O-BISTREN by virtue of the fact that it contains only two quite basic NH groups on each end separated by an NH group with somewhat lower basicity. Building pyridine moieties into the O-BISDIEN ligands as indicated by **3** and **4** lowers the basicity considerably because the pyridine nitrogen has relatively low basicity. C-BISTREN, **5**, which contains a  $\text{CH}_2$  group in place of the ether oxygen in the bridging moieties of O-BISTREN has a rather complex behavior which will be described in detail below.

#### COMPLEXES FORMED BY MACROCYCLIC AND MACROBICYCLIC LIGANDS 1-5 WITH TRANSITION METAL IONS

The stability constants of various copper complexes of these ligands are listed in Table 1 (ref. 4, 5), as an example of the interactions of these ligands with transition metal ions. It is interesting to note that the mononuclear copper complexes have three protonated forms in all cases except where one of the donor groups is a pyridine moiety, in which case only two protonated species are formed. Although thermodynamics gives us no structural information on these complex species it is logical to assume that the protons are on one end of the molecule while the metal is coordinated to the donor groups at the other end. Where one of the donor groups is a pyridine nitrogen the basicity is so low as to not be measurable by potentiometric means. It is seen that the protonation constants of the mononuclear complex indicate that C-BISTREN is more basic than O-BISTREN. This is no doubt due to the electron withdrawing effect of the ether oxygen in O-BISTREN which is replaced by a  $\text{CH}_2$  group in C-BISTREN. It is also noted that the pyridine nitrogen lowers the basicity of the macrocyclic ligands so that O2-BISBAMP and O1-BISBAMP are less basic than the parent compound O-BISDIEN. Therefore, their metal ion affinities would be expected to be less as is observed in both the mononuclear and binuclear complexes. The copper ion affinity of O-BISDIEN is lower than that of O-BISTREN by virtue of the fact that it contains fewer basic nitrogens. It is probably not as much lower as would be expected due to two factors: first the central nitrogen of O-BISDIEN is not as poor a donor as the central nitrogen of O-BISTREN. Also the O-BISDIEN macrocycle is much more flexible and can probably accommodate to the coordination sphere of the metal ion more readily than the macrobicyclic ligand O-BISTREN.

**Table 1.** Logarithms of Equilibrium Constants<sup>a</sup> of Cu(II) Complexes of O-BISTREN, C-BISTREN, O-BISDIEN, O1-BISBAMP, and O2-BISBAMP

Equilibrium Quotient, Q	Log Q				
	<b>2</b> <sup>b</sup>	<b>5</b>	<b>1</b>	<b>3</b>	<b>4</b>
$[\text{MH}_3\text{L}]/[\text{MH}_2\text{L}][\text{H}]$	5.20	7.62	3.45	-	-
$[\text{MH}_2\text{L}]/[\text{MHL}][\text{H}]$	7.14	8.70	7.46	5.24	6.19
$[\text{MHL}]/[\text{ML}][\text{H}]$	7.92	10.08	8.01	7.44	7.04
$[\text{ML}]/[\text{M}][\text{L}]$	17.69	15.39	16.46	15.19	14.81
$[\text{M}(\text{OH})\text{L}][\text{H}]/[\text{ML}]$	-	-	-10.63	-9.70	-10.0
$[\text{M}_2\text{L}]/[\text{M}]^2[\text{L}]$	28.32	28.76	27.30	24.01	25.76
$[\text{M}_2(\text{OH})\text{L}][\text{H}]/[\text{M}_2\text{L}]$	-3.89	-7.59	-6.51	-6.5	-6.5
$[\text{M}_2(\text{OH})_2\text{L}][\text{H}]/[\text{M}_2(\text{OH})\text{L}]$	-	-10.81	-10.40	-9.12	-9.4

<sup>a</sup>  $\mu = 0.100 \text{ M (KNO}_3\text{)}$ ;  $T = 298.15 \text{ K}$ . <sup>b</sup>  $\mu = 0.100 \text{ M (NaClO}_4\text{)}$ .

It is noted that in spite of the greater basicity of the donor groups of C-BISTREN its affinity for the copper ion in the formation of the mononuclear complex is much lower than that of O-BISTREN. However, this deficiency is overcome in the formation of the binuclear complex for which that of C-BISTREN is higher than that of O-BISTREN. This has been interpreted as an indication of the lack of pre-organization of the ligand C-BISTREN, for which the carbon atoms would tend to lie close together through hydrophobic bonding, and are therefore not pre-organized for metal ion coordination. This shows up primarily in the first metal binding constant because hydrophobic bonding would have to be overcome and the ligand would have to open up to form a complex. The greater basicity of the remaining nitrogens of the ligand would be obvious in the second binding constant so that the stability constant of the binuclear complex is somewhat

higher. Thus the formation of these complexes can be viewed as involving two effects: 1, the greater basicity of the C-BISTREN nitrogens and 2, its lack of pre-organization, with the former slightly overcoming the latter effect. Also the lower basicity of the pyridine nitrogens can be seen in the fact that the stability constants of O1-BISBAMP and O2-BISBAMP are lower than the corresponding constant of O-BISDIEN. The electron-withdrawing effect of the four ether oxygens of O2-BISBAMP, compared to the two ether oxygens of O1-BISBAMP can be seen in the lower stability of the copper complex formed with O2-BISBAMP. The fact that its binuclear complex is more stable than that of the binuclear complex of O1-BISBAMP is interesting and has been ascribed to the repulsion between the metal ions which would be much lower in O2-BISBAMP because the metal ions can be farther apart in this complex. This effect apparently overcomes the reverse electron-withdrawing effects of the ether oxygens.

It is seen that the binuclear copper complexes of all five ligands have considerable affinity for the hydroxyl ion, as indicated by the  $pK$ 's listed in Table 1. The highest  $pK$  showing the lowest affinity is that of C-BISTREN probably because of its intrinsic affinity for the copper ion. It is higher than that of the other ligands shown which have electron-withdrawing ether oxygens. The lowest  $pK$ , indicating the highest binding constant, is that of Cu(II)-O-BISTREN. Here the additional affinity has been ascribed to the hydrogen bonding that can occur between the bridging OH ion and one of the ether oxygens of the bridges in the macrocycle. The correctness of this suggestion has been indicated by the crystal structure of the hydroxo-bridged dicopper O-BISTREN complex which is indicated in Figure 1. In all these hydroxo binuclear copper complexes of the macrocyclic and macrobicyclic ligands 1 through 5 are considered to have bridging hydroxyl ions in which the OH<sup>-</sup> ion is coordinated to both metal centers simultaneously.

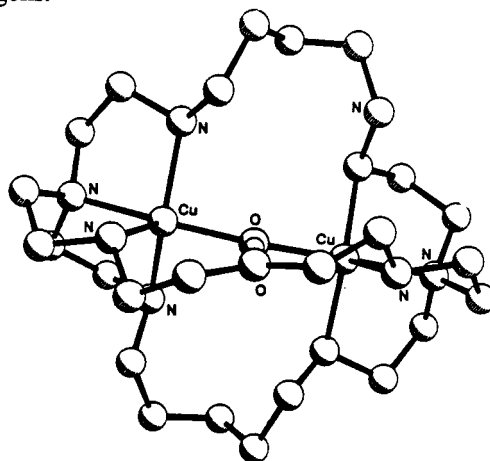


Figure 1. Diagram illustrating structure of hydroxo-bridged dicopper(II)-O-BISTREN cryptate showing proximity of OH to an ether oxygen of the ligand.

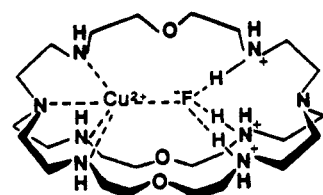
#### COMPLEXES WITH SIMPLE BRIDGING GROUPS

A number of O-BISTREN and O-BISDIEN complexes have been described in which the protonated mononuclear and binuclear complexes of these ligands combined with various bridging anions (refs. 6-9). An interesting example of the bridging of negative ions between metal centers has been described by Motekaitis et al. (ref. 5) in which the affinities of O-BISTREN and C-BISTREN for the hydroxide and fluoride ions are compared. It is seen that the binding of fluoride ion to these two cryptands is much weaker than the binding of hydroxide ion. This can be seen in the relative  $pK$ 's of HF and H<sub>2</sub>O, so that although the two bridging anions are isoelectronic, the hydroxide ion can be expected to be much more basic than the fluoride ion. The fluoride binding to O-BISTREN and C-BISTREN is described in Table 2 (ref. 5), in which it is seen that in the mononuclear complexes the fluoride ion bridges between the metal center on one side of the ligand and the various protonated forms of the ligand on the other side through hydrogen bonding. In the binuclear cryptand there can be no question of the bridging of the fluoride ion to the two metal centers because of the fact that only one fluoride ion is coordinated. It is seen that in all cases the bridging of the fluoride ion is weaker in C-BISTREN than it is in O-BISTREN. This is considered to be a consequence of the stronger binding of C-BISTREN for the metal centers making the additional coordination provided by the bridging group somewhat weaker. In this case the bridging fluoride ion cannot have the stabilizing effect of hydrogen bonding to the ether oxygens of the bridge so the comparison between O-BISTREN and

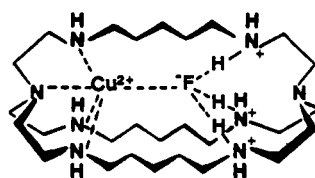
Table 2. Bridging of Fluoride by Binuclear and Mononuclear Cu(II) Complexes of O-BISTREN and C-BISTREN

Equilibrium Quotient, Q	Log Q <sup>a</sup>	
	O-BISTREN	C-BISTREN
[MH <sub>3</sub> FL]/[MH <sub>3</sub> L][F]	4.1	3.4
[MH <sub>2</sub> FL]/[MH <sub>2</sub> L][F]	3.0	2.7
[MHFL]/[MHL][F]	2.7	2.1
[M <sub>2</sub> FL]/[M <sub>2</sub> L][F]	4.5	3.3

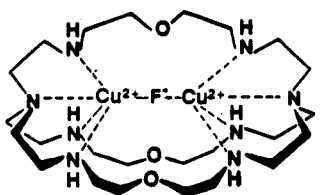
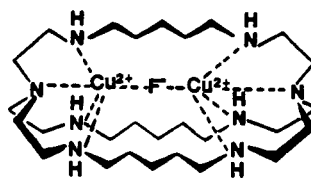
<sup>a</sup>  $\mu = 0.100$  M (0.090 M NaClO<sub>4</sub> + 0.010 M NaF); T = 298.15 K.



6 mononuclear F O-BISTREN



7 mononuclear F C-BISTREN

8  $[\text{Cu}_2\text{LF}]^{3+}$  (L = O-BISTREN)9  $[\text{Cu}_2\text{L}'\text{F}]^{3+}$  (L' = C-BISTREN)

C-BISTREN in this case depends on the relative affinities of the two cryptand ligands for the metal ions. The bridging of the fluoride ion between protonated nitrogens (by hydrogen bonding) and the metal centers in indicated by formulas 6-9.

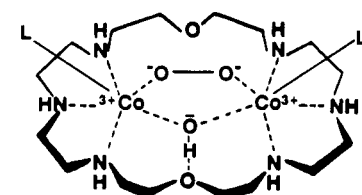
### DIOXYGEN COMPLEXES

The dioxygen in a binuclear cobalt macrocyclic or macrobicyclic complex may be considered a negative bridging group, since it is usually pictured as a  $\mu$ -peroxo group bound to two cobalt centers that are +3 in charge. Actually we understand that the coordinated dioxygen is somewhere in between the charge of the peroxo group and of neutral dioxygen. Also the cobalt is not really Co(III) but has a higher charge than Co(II) and is a better coordinator for that reason. The binuclear cobalt dioxygen complexes formed from O-BISTREN, O-BISDIEN and O1-BISBAMP are compared in Table 3 (ref. 10). It is seen that in all cases dioxygen complex formation occurs

**Table 3.** Logarithms of the Oxygenation Constants of Co(II) Complexes with BISDIEN, O-BISTREN, and O1-BISBAMP

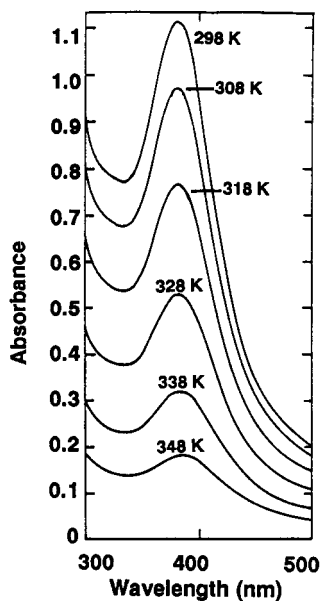
Equilibrium Quotient, Q	log $Q^a$		
	O-BISTREN	BISDIEN	O1-BISBAMP
$[\text{M}_2\text{LO}_2(\text{OH})][\text{H}]/[\text{M}_2\text{L}]\text{PO}_2$	-6.0	-3.29	-8.70
$[\text{M}_2\text{LO}_2(\text{OH})_2][\text{H}]/[\text{M}_2\text{LO}_2(\text{OH})]$		-8.25	-7.63
$[\text{M}_2\text{LO}_2(\text{OH})_3][\text{H}]/[\text{M}_2\text{LO}_2(\text{OH})_2]$		-9.36	-9.45

<sup>a</sup>  $\mu = 0.10 \text{ M}$ ,  $T = 298.15 \text{ K}$ ,  $P_{\text{O}_2} = 1.0 \text{ atm}$

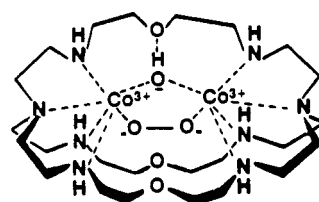


10  $\mu$ -hydroxo- $\mu$ -dicobalt chelate of O-BISDIEN chelate

with the simultaneous formation of a hydroxide bridge. However, O-BISDIEN and O1-BISBAMP have dihydroxo and trihydroxo forms of the oxygen complex while O-BISTREN does not. This is in accordance with the fact that the oxygen complexes formed by the former two ligands have coordinate bonding similar to that indicated by formula 10 in which the L groups are probably water molecules donated by the solvent. Conversion of the L donors to hydroxide groups one at a time occurs at higher pH. In the case of O-BISTREN the oxygen complex formed is already six-coordinate and there is no possibility of forming higher hydroxo forms of this complex. If one considers the oxygen complexes initially formed it is obvious from the data in Table 3 that the O-BISDIEN dioxygen complex has the highest stability followed by a sharp drop for the oxygen complex of O-BISTREN and a further drop in stability for the O1-BISBAMP complex. The lower stability of the O1-BISBAMP binuclear cobalt complex compared to analogous O-BISDIEN complex is understandable in view of the lower basicity of the pyridine nitrogen. However, the metal ion in the O-BISTREN complex is more completely coordinated than the cobalt complexes of the other two ligands. One would expect therefore, that the O-BISTREN complex would be more stable than that of O-BISDIEN and actually it is much less stable. The interpretation given this fact is that probably the cryptand ligand in O-BISTREN has to distort considerably in order to form the oxygen complex. Until the crystal structure becomes available this is probably the most reasonable interpretation.



**Figure 2.** UV-visible absorbance of the equilibrium system for the oxygenation of  $\mu$ -hydroxo-dicobalt(II) O-BISTREN.  $P_{O_2} = 1.00$  atm., for the temperatures indicated.  $L = 1/2[Co] = 2.00 \times 10^{-4}$  M,  $\mu = 0.100$  M KCl; pH = 8.6



**11**  $\mu$ -hydroxo- $\mu$ -dicobalt chelate of O-BISTREN chelate

The fact that the oxygen complex of dicobalt O-BISTREN, **11**, is very labile at room temperature, added to the fact that the ligand is not readily degraded, makes the hydroxo cobalt O-BISTREN cryptate an ideal oxygen carrier. Figure 2 (refs. 11,12) shows the absorption spectra of the oxygen complex formed as a function of temperature. Since intensity of the spectra indicates the degree of oxygen complex formation it is seen that there is considerable difference in degree of formation between 298 K (approximately room temperature) and 348 K. At even higher temperature the oxygen complex disappears completely but it is formed again when the temperature is lowered. With the intensity of the spectra bands in Figure 2, the enthalpy of formation was found to be  $-52.7$  kJ/mol per mole and the entropy was found to be strongly negative with a value of  $-127$  J/mol K. Thus oxygen complex formation is driven by the enthalpy of reaction but at higher temperatures, of course, it is highly dissociated.

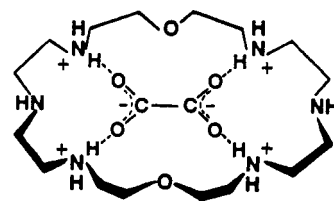
#### AFFINITIES OF BRIDGING BIDENTATE LIGANDS FOR BINUCLEAR COBALT O-BISDIEN COMPLEXES

The presence of two free coordination sites on the bis-dicobalt O-BISDIEN hydroxo bridged and peroxy bridged dioxygen complex, **10**, indicated the possibility of combining this complex with another bridging ligand that would coordinate simultaneously both metal centers through the open positions. The first example of a bridging ligand to be considered is the oxalate ion, which combines not only with the dioxygen complex but with the bis-cobalt binuclear O-BISDIEN complex, the mononuclear protonated O-BISDIEN complex, and the polyprotonated O-BISDIEN itself. These equilibria were measured potentiometrically in three stages, involving the interaction of oxalate ion with O-BISDIEN, with the mononuclear O-BISDIEN complex, and the binuclear O-BISDIEN complex all under nitrogen. The equilibrium constants thus determined are indicated in Table 4 and examples of some of the complexes

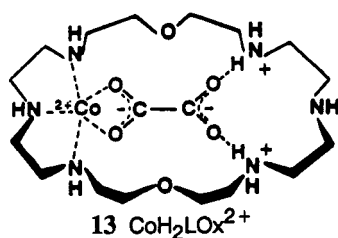
**Table 4.** Log Oxalate Formation Constants<sup>a</sup> with BISDIEN and Co(II)-BISDIEN Complexes

Quotient	Q Values		
	Cu <sup>2+</sup>	Co <sup>2+</sup>	Other
$[MLHOx]/[MLH][Ox]$	3.33	4.36	
$[MLH_2Ox]/[MLH_2][Ox]$	3.76	6.50	
$[MLH_3Ox]/[MLH_3][Ox]$	5.29		
$[MLH_4Ox]/[MLH_4][Ox]$	3.25		
$[M_2LOx]/[M_2L][Ox]$	5.79	9.06	
$[M_2L(OH)Ox]/[M_2L(OH)][Ox]$	3.18		
$[H_6LOx]/[H_6L][Ox]$			4.68
$[H_5LOx]/[H_5L][Ox]$			3.59
$[H_4LOx]/[H_4L][Ox]$			2.06

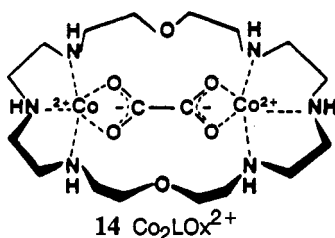
<sup>a</sup>  $\mu = 0.100$  M (KCl); T = 298.15 K.



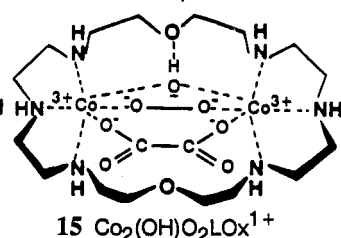
**12**  $H_4LOx^{2+}$



**13**  $CoH_2LOx^{2+}$



**14**  $Co_2LOx^{2+}$



**15**  $Co_2(OH)O_2LOx^{1+}$

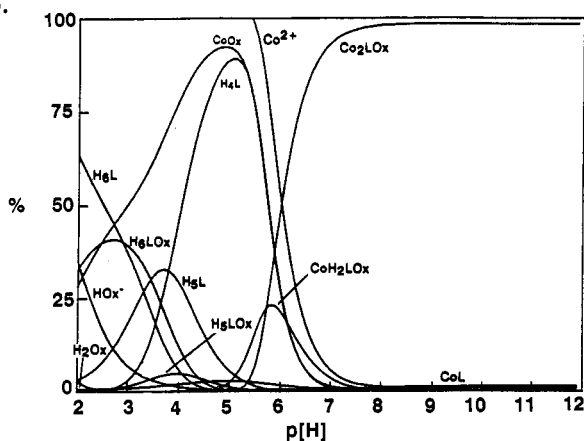
formed are indicated by formulas 12-14. With the use of these equilibrium constants any additional interaction with oxalate with oxygen present can be measured potentiometrically. Since the equilibrium constant between the binuclear cobalt O-BISDIEN complex and oxygen is already known (Table 2) the potentiometric measurements under dioxygen can give not only the binding constant of oxygen with the oxalato bridged binuclear O-BISDIEN complex but also the binding constant of oxalate with the hydroxo bridged peroxo bridged dioxygen complex of binuclear cobalt O-BISDIEN (ref. 13, 14). These constants are indicated by equations (1) and (2)

$$[\text{Co}_2(\text{OH})(\text{O}_2)(\text{OxL})][\text{H}^+]/[\text{Co}_2(\text{Ox})\text{L}]\text{P}_{\text{O}_2} = 10^{-7.92} \text{ M atm}^{-1} \quad (1)$$

$$[\text{Co}_2(\text{OH})(\text{O}_2)(\text{Ox})\text{L}]/[\text{Co}_2(\text{OH})(\text{O}_2)\text{L}][\text{Ox}] = 10^{4.43} \text{ M}^{-1} \quad (2)$$

where L = O-BISDIEN and Ox = oxalate anion

The ability of this oxalato- and hydroxo-bridged dioxygen complex, 15, to predominate over the competing dioxygen species and the competing oxalato bridged species is best indicated by the distribution function shown in Figure 3, which shows that the oxalato bridged dioxygen complex predominates at around pH 8.5 with a maximum concentration that indicates about 65% of the macrocyclic ligand O-BISDIEN is tied up in this species at this particular pH. Therefore redox reactions of this species in which the oxalate reduces the dioxygen peroxo bridge is best carried out at pH 8.5.



**Figure 3.** Distribution of species as a function of pH for a solution containing a 1:1:2 molar ratio of BISDIEN-oxalate-Co(II) at 298.15 K,  $\mu = 0.100 \text{ M}$  under 1 atm oxygen:  $[\text{O-BISDIEN}] = 0.00100 \text{ M}$ .

Other bidentate bridging groups which are recognized by the cobalt dioxygen complex of O-BISDIEN include keto-malonate (ref. 15), catecholate, tironate (ref. 16), malonate and glycinate (ref. 17). The formation constants have been obtained potentiometrically for the mixed complexes containing both the peroxo bridge and the bridging bidentate ligand. Ultimately it is planned to investigate the redox reactions between the coordinated dioxygen and the secondary bridging ligands which are also reducing agents. Such reactions have already been investigated for the oxalate and keto-malonate (mesoxalate) binuclear Co(II)-BISDIEN complexes.

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#### REFERENCES

1. A. E. Martell, *J. Inclus. Phenomena*, **7**, 99-106 (1989).
2. A. E. Martell, *Adv. Supramol. Chem.*, **1**, 145-197 (1990).
3. A. E. Martell, In *Crown Compounds: Toward Future Applications*, S. R. Cooper, Ed., VCH, New York, (1992) pp.99-134.
4. R. Menif, D. Chen and A. E. Martell, *Inorg. Chem.*, **28**, 4633 (1989).
5. R. J. Motekaitis, A. E. Martell, I. Murase, J. M. Lehn and W. M. Hosseini, *Inorg. Chem.*, **27**, 3630-3636 (1988).
6. R. J. Motekaitis, A. E. Martell, J. M. Lehn and E. I. Watanabe, *Inorg. Chem.*, **21**, 4253-4257 (1982).
7. R. J. Motekaitis, A. E. Martell, J. P. Lecomte and J. M. Lehn, *Inorg. Chem.*, **22**, 609-624 (1983).
8. R. J. Motekaitis, A. E. Martell, B. Dietrich and J. M. Lehn, *Inorg. Chem.*, **23**, 1588-1591 (1984).
9. R. J. Motekaitis, A. E. Martell and I. Murase, *Inorg. Chem.*, **25**, 938-944 (1986).
10. M. G. Basallote and A. E. Martell, *Inorg. Chem.*, **27**, 4219 (1988).
11. R. J. Motekaitis and A. E. Martell, *J. Chem. Soc. Chem. Commun.*, 1020-1022 (1988).
12. R. J. Motekaitis and A. E. Martell, *J. Am. Chem. Soc.*, **110**, 7715-7719 (1988).
13. A. E. Martell and R. J. Motekaitis, *J. Chem. Soc. Chem. Commun.*, 915-916 (1988).
14. A. E. Martell and R. J. Motekaitis, *J. Am. Chem. Soc.*, **110**, 8059-8064 (1988).
15. R. J. Motekaitis and A. E. Martell, *Inorg. Chem.*, **30**, 694-700 (1991).
16. B. Szpoganicz, R. J. Motekaitis and A. E. Martell, *Inorg. Chem.*, **29**, 1467-1474 (1990).
17. R. J. Motekaitis and A. E. Martell, *Inorg. Chem.*, in press.