Molecular Recognition and Host–Guest Interactions in Complexes of O-Bistren, C-Bistren, and Bisdien

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Abstract. The host–guest relationships of the complexes of the cryptand ligands O-BISTREN and C-BISTREN, and of the analogous macrocyclic ligand BISDIEN are compared. The affinities of their binuclear copper(II) complexes for the bridging ligands (OH^-, F^-) as 'cascade' type guests (i.e., guests of guests) are reported. The ability of the dicobalt(II)-BISDIEN complex to coordinate dioxygen and an additional bifunctional guest simultaneously, leads to the possibility of a new type of catalysis occurring within the cavity of a macrocyclic complex.

Key words. Cryptand, copper(II) complexes, catalysis, cobalt(II) complexes.

1. Introduction

The ability of macrocyclic and macrobicyclic ligands to function as hosts in binding metal ions and anions as guests depends on their structures, in particular their degree of preorganization [1], and on the nature of the donor atoms, as well as on the nature of guests. In this paper the macrobicyclic (cryptand) polyamine ligands O-BISTREN, **1**, and C-BISTREN, **2**, and the macrocyclic ligand BISDIEN, **3**, are compared with respect to how protonation and metal ion coordination influence the degree of molecular recognition of the host for various donor ions and molecules as
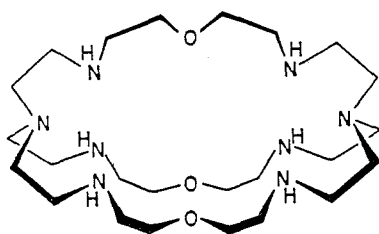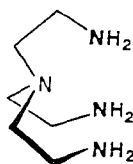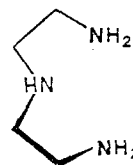

1 O-BISTREN
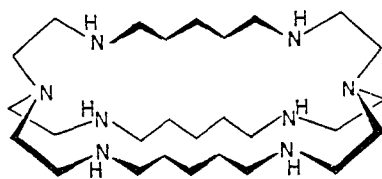
2 C-BISTREN
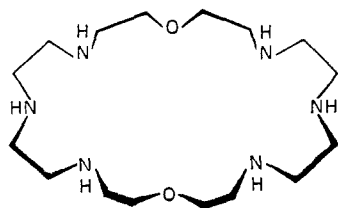
3 BISDIEN

4 TREN

5 DIEN

guests. The formulas of the free bases of **1–3** are compared with the formulas of their coordinating components, TREN and DIEN, represented by **4** and **5**, respectively.

2. Discussion

2.1. BASICITIES OF THE LIGANDS

The protonation constants of ligands **1–5**, listed in Table I, show interesting trends related to their conformations. The non-cyclic polyamines TREN, **4**, and DIEN, **5**, generally have higher second and third protonation constants than do the corresponding moieties in the cryptand and macrocyclic ligands because of reduced charge repulsions resulting from the fact that their conformations in solution are not restricted by ring formation, and assume more extended structures than those

Table I. Protonation constants and metal ion stability constants of O-BISTREN, C-BISTREN, TREN, BISDIEN and DIEN; $\mu = 0.100$ M (NaClO$_4$), $t = 25.0$°C.

Equilibrium quotient Q	Log Q				
	O-BISTREN [2, 3, 4]	C-BISTREN [5]	TREN [2]	BISDIEN [6]	DIEN [6]
$\dfrac{[HL^+]}{[H^+][L]}$	9.99	10.35	10.12	9.65	9.84
$\dfrac{[H_2L^{2+}]}{[H^+][HL^+]}$	9.02	9.88	9.41	8.92	9.02
$\dfrac{[H_3L^{3+}]}{[H^+][H_2L^{2+}]}$	7.98	8.87	8.47	8.30	4.23
$\dfrac{[H_4L^{4+}]}{[H^+][H_3L^{3+}]}$	7.20	8.38		7.64	
$\dfrac{[H_5L^{5+}]}{[H^+][H_4L^{4+}]}$	6.40	8.14		3.81	
$\dfrac{[H_6L^{6+}]}{[H^+][H_5L^{5+}]}$	5.76	7.22		3.26	
$\dfrac{[CuL^{2+}]}{[Cu^{2+}][L]}$	17.59	15.39		16.46	15.9
$\dfrac{[Cu_2L^{4+}]}{[CuL^{2+}][Cu^{2+}]}$	10.73	13.37		10.84	
$\dfrac{[Cu_2(OH)L^{3+}][H^+]}{[Cu_2L^{4+}]}$	-3.8	-7.59		-6.51	
$\dfrac{[CoL^{2+}]}{[Co^{2+}][L]}$	11.20			9.73	8.0
$\dfrac{[Co_2L^{4+}]}{[CoL^{2+}][Co^{2+}]}$	5.60			2.7	
$\dfrac{[Co_2(OH)L^{3+}][H^+]}{[Co_2L^{4+}]}$	-7.20				

shown in formulas **1–5**. The lower basicities of the amino groups of O-BISTREN relative to C-BISTREN are due to the electron-withdrawing effects of the three ether oxygens in the bridging groups of the former.

2.2. BINUCLEATING TENDENCIES OF O-BISTREN, C-BISTREN, AND BISDIEN

Because of the greater flexibility of BISDIEN, its binucleating tendencies with various metal ions are much weaker than those of the macrobicyclic ligands. The stability constants of the 1 : 1 Cu(II) and Co(II) complexes of BISDIEN are considerably higher than those of DIEN, indicating that more than three amino nitrogens of BISDIEN are coordinated to the metal ion, and the ligand probably has folded conformations in which from four (for Cu(II)) to six (for Co(II)) amino groups are coordinated [6]. Therefore it is understandable that while there is a considerable tendency for coordination with a second metal ion to form a dinuclear complex in the case of Cu(II), which effectively coordinates strongly only four amino groups, the analogous tendency for divalent transition metal ions which form octahedral complexes is very weak ($10^{2.7}$ for Co(II), and much lower for Ni(II) [6]). Binuclear complexes of BISDIEN are strongly stabilized by appropriate coordinating bridging groups, such as ethylenediamine, hydroxide ion, imidazolate ion (for Cu(II)), and dioxygen (for Co(II)) [6].

The macrobicyclic ligands O-BISTREN and C-BISTREN, on the other hand, show strong binucleating tendencies, with or without suitable coordinating bridging groups. This characteristic tendency to function as hosts for two metal ions as guests is considered to be due to preorganization which provides two tetramine cavities at opposite ends of the macrobicyclic octamine cryptand. It has been pointed out [5] that the cavity in the C-BISTREN structure seems to be less preorganized than that of O-BISTREN, probably because of the tendency of the pentamethylene bridges to self-associate through hydrophobic bonding.

In aqueous solution, in the absence of bifunctional coordinating bridging groups, the dicopper(II) complexes of both O-BISTREN and C-BISTREN polarize an internal coordinated water molecule to produce a μ-hydroxo bridge. The corresponding hydrolysis constants are very much higher (higher OH^- affinity; lower pK) than those of analogous mononuclear complexes, reflecting the very strong polarizing power of two metal ions on a bridging water molecule.

There is an interesting reversal in the relative magnitudes of the successive Cu(II) binding constants of O-BISTREN and C-BISTREN. The latter has more basic donor groups and would be expected to form more stable metal complexes; however its 1 : 1 complex with Cu(II) is considerably weaker than that of O-BISTREN. On the other hand its second metal binding constant is much stronger than that of O-BISTREN with the result that the overall binding constant ($\beta = [M_2L/[M]^2[L]]$) is somewhat larger for C-BISTREN. The interpretation given to this behavior [5] involves differences in the preorganization of the ligands. Coordination of the first metal ion by C-BISTREN would require opening up of the cryptand cavity and disruption of the hydrophobic bonding associations of the hydrocarbon bridges. Thus the ligand would be prepared (preorganized) for coordination of the second metal ion, which would take place with a relatively high stability constant. Overall, formation of the dinuclear copper(II) C-BISTREN cryptate complex involves two

effects operating in opposite directions, the breaking up of hydrophobic bonding, which cost energy, and the greater basicity of the amino groups, which favors higher stability, with the latter effect predominating.

2.3. REACTIONS OF BINUCLEAR CU(II) COMPLEXES WITH COORDINATING BRIDGING GROUPS

The binding constants of (isoelectronic) hydroxide and fluoride ions to the binuclear Cu(II) complexes of O-BISTREN and C-BISTREN are presented in Table II.

Table II.   Binding constants of hydroxide and fluoride ions with dinuclear Cu(II) complexes of O-BISTREN and C-BISTREN: $\mu = 0.100$ M (NaClO$_4$), $t = 25.0°$C.

Equilibrium quotient, Q	Log Q	
	O-BISTREN	C-BISTREN
$\dfrac{[Cu_2(OH)L^{3+}]}{[Cu_2L^{4+}][OH^-]}$	10.0	6.19
$\dfrac{[Cu_2FL^{3+}]}{[Cu_2L^{4+}][F^-]}$	4.5[a]	3.3[a]

[a] $\mu = 0.100$ M (0.090 M NaClO$_4$ + 0.010 M NaF).

The higher basicities of the amino groups in C-BISTREN would be expected to produce stronger Cu—N coordinate bonds, and therefore weaker coordinate bonds to secondary ligands such as F$^-$ and OH$^-$. The fluoride ion is seen to behave normally, with about a factor of ten difference in its binding constants, with Cu$_2$O-BISTREN^{4+} having the higher affinity for the fluoride anion (Table II, formulas 6 and 7).
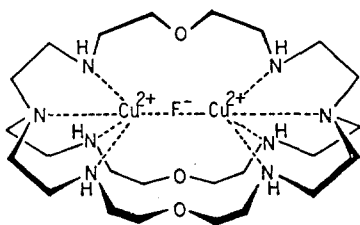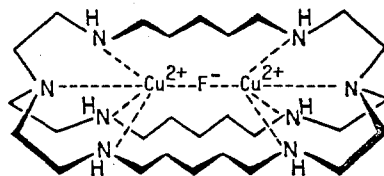
6 [Cu$_2$LF]$^{3+}$ L = O-BISTREN   7 [Cu$_2$L'F]$^{3+}$ L' = C-BISTREN

This interpretation, however, does not explain the fact that the affinity of Cu$_2$O-BISTREN^{4+}, 8, for OH$^-$ ion is nearly four orders of magnitude greater than that of Cu$_2$C-BISTREN^{4+}, 9. Therefore, it was concluded that the former has a structure which provides stabilization not available to the latter. It was suggested [2] that the high stability of the hydroxo bridge of the dicopper(II) complex of O-BISTREN is due to hydrogen bonding to one of the ether bridging groups, an interaction which is not possible with the fluoride-bridged complex, as indicated by
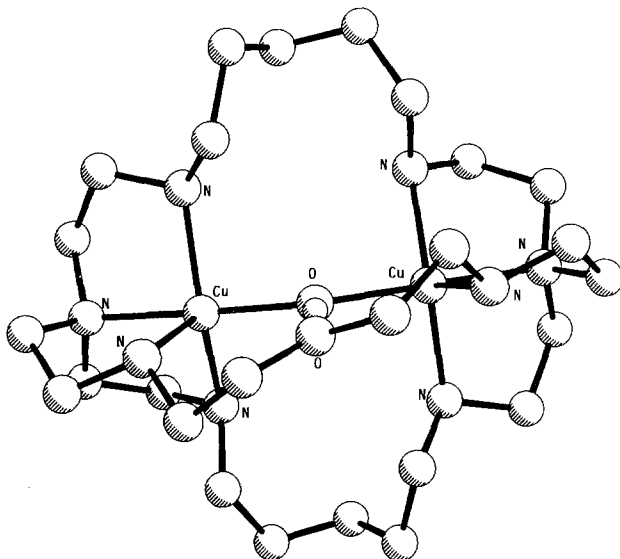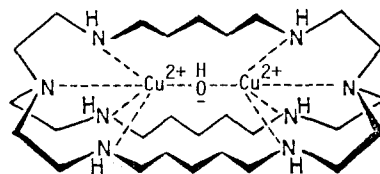
Fig. 1.   Diagram illustrating structure of hydroxo-bridged dicopper(II)-O-BISTREN cryptate showing bent Cu—O—Cu bridge and proximity of OH to an ether oxygen of the ligand.

formulas **6** and **8**. Recently, it has been found possible to crystallize the hydroxo bridged complex and determine its structure by X-ray crystallography [7]. Figure 1, which is a drawing of the structure based on the crystallographic parameters obtained, confirms the hydrogen bonding of the hydroxo bridge to an ether oxygen, with a bent Cu-OH-Cu angle.
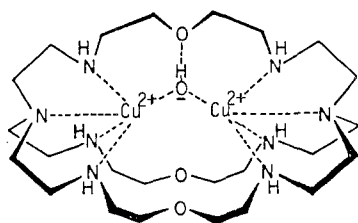
8 $[Cu_2(OH)L]^{3+}$ L = O-BISTREN   **9** $[Cu_2(OH)L']^{3+}$ L' = C-BISTREN

The unusually high stability of the hydroxo-bridged dinuclear cryptate of Cu(II)-O-BISTREN has a profound influence on the nature of the complex species formed in solution. Figure 2 is a distribution diagram of the individual complex species formed as a function of pH in a solution containing a 1 : 1 ratio of the molar concentrations of O-BISTREN and Cu(II) ion. It is seen that in spite of the unfavorable concentration ratio, the binuclear complex predominates in its hydroxo-bridged form over most of the pH range. In this solution, uncoordinated ligand in various stages of protonation are seen to also be present.
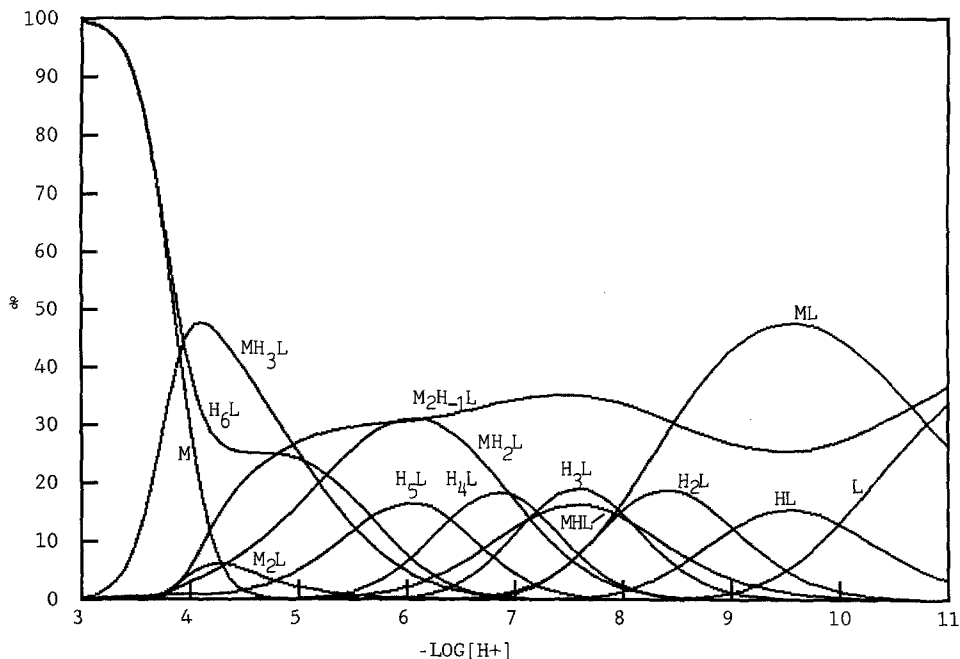
Fig. 2. Distributions of species as a function of p[H] in a solution containing a 1 : 1 molar ratio of O-BISTREN to copper(II) in 0.100 M NaClO$_4$ and 25.0°C. Component concentrations, H$_6$Bistren^{6+} 1.00 × 10^{-3} M; Cu^{2+}, 9.98 × 10^{-4} M.

2.4. DIOXYGEN COMPLEXES

The differences in stabilities of the dioxygen adducts of the dinuclear cobalt complexes of O-BISTREN and BISDIEN also deserve comment. The higher basicities of the eight amino groups of O-BISTREN over those of the six amino groups of BISDIEN would lead to the expectation of much higher dioxygen affinity of the former over the latter [8]. It turned out, however, that the oxygenation constant associated with the formation of **10** is about three orders of magnitude lower than that of **11**. The explanation offered for this interesting reversal of the expected relative magnitudes of the oxygenation constants was based on possible steric crowding in the cavity of **10**, which interferes with metal—dioxygen bond formation. This complex turns out to be of interest for oxygen separation processes because of its rapid reversibility at moderate temperatures [9].

It is noted that the dioxygen complex of dicobalt BISDIEN, **11**, indicates only five coordinated bonds between each metal ion and the donor groups indicated. Because of the Co(III)-like nature of the metal ion, it is expected to be 6-coordinate, so that two water molecules (one for each metal) are probably present in the coordination spheres of the metal ions in **11**. This interpretation has been confirmed [6] by the hydrolysis of this complex in two steps to give di- and trihydroxo dioxygen complexes with pK's of 8.25 and 9.36 [6]. In addition to hydrolysis (hydrogen ion dissociation) it should be possible to coordinate additional donor groups, including bifunctional bridging groups, to the aquo sites. This concept has
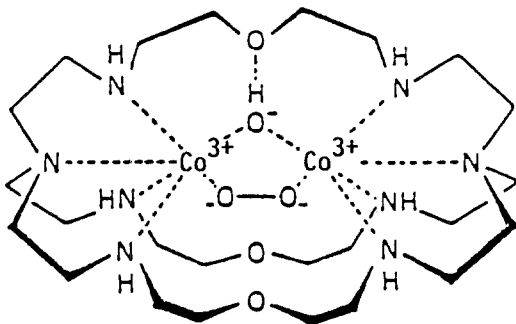
10 Suggested arrangement of coordinate bonds in dibridged dioxygen complex formed from dinuclear Co(II) O-BISTREN cryptate

recently been confirmed by the coordination of a reducing bridging group, the oxalate ion, giving an intermediate dioxygen complex, indicated by **12**, which undergoes facile electron transfer from oxalate to coordinated peroxo to give carbon dioxide and water [10]. The activation of coordination dioxygen in the cavity of the dinuclear macrocyclic complex **12** so as to react with a coordinated reductant in the same complex molecule is the first such reaction to be reported. Further studies in this laboratory are being directed toward catalysis of redox reactions involving coordinated dioxygen and coordinated substrates within the cavities of dinuclear macrocyclic complexes.
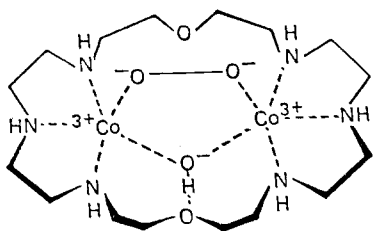
11 μ-Hydroxo-μ-peroxodicobalt BISDIEN chelate
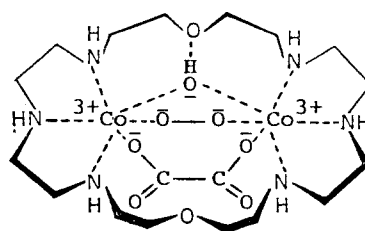
12 μ-Hydroxo-μ-oxalato-μ-peroxo dicobalt BISDIEN chelate

3. Conclusions

The results of the research described above makes possible the following general conclusions.

1. Hydroxide ion is more strongly bound than fluoride ion as bridging donor groups (guests) in hosts consisting of dinuclear copper(II) cryptates of O-BISTREN and C-BISTREN.
2. The cavities of binucleating cryptands seem to be less preorganized with hydrocarbon bridges between the coordinating moieties.

3. The presence of an electronegative atom in the bridging linkages of binucleating cryptands greatly increases the binding of a bridging hydroxide ion through hydrogen bonding.
4. The greater flexibility of a binucleating macrocyclic ligand relative to an analogous macrobicyclic cryptand makes possible stronger binding of bifunctional bridging guests such as imidazolate and dioxygen.
5. The simultaneous coordination of two potentially reactive bridging guests in binuclear host complexes may produce strong catalytic effects on the guest molecules or ions.

Acknowledgement

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