Inorg. Chem. **1988**, *27*, 3630-3636

Contribution from the Departments of Chemistry, Texas A&M University, College Station, Texas 77843, and Institut Le Bel, Universite Louis Pasteur, 67000 Strasbourg, France

Comparative Study of the Copper(II) Cryptates of C-BISTREN and O-BISTREN. Protonation Constants, Formation Constants, and Secondary Anion Bridging by Fluoride and Hydroxide[†]

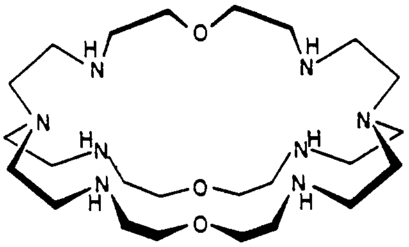
Ramunas J. Motekaitis, Arthur E. Martell,* Ichiro Murase, Jean-Marie Lehn, and Mir Wais Hosseini

Received February 22, 1988

Potentiometric equilibrium measurements of hydrogen ion concentrations have been employed for the determination of protonation constants and Cu(II) stability constants of the macrobicyclic ligand C-BISTREN (1,4,10,13,16,22,27,33-octaazabicyclo[11.11.11]pentatriacontane) at 25.0 °C in solutions maintained at 0.10 M ionic strength by the addition of sodium perchlorate with and without a 0.010 M concentration of sodium fluoride. The results are compared with the corresponding equilibrium constants previously reported for O-BISTREN (7,19,30-trioxa-1,4,10,13,16,22,27,33-octaazabicyclo[11.11.11]pentatriacontane). The measurements made in the absence of fluoride provide six protonation constants of the ligands, the stability constants of mononuclear and binuclear Cu(II) complexes, the protonation constants of the mononuclear copper(II) cryptates, and the hydroxide-bridging constants of the binuclear copper(II) cryptates. Potentiometric measurements of the ligands in the $NaClO_4$–NaF medium provide equilibrium constants for bridging of the bifluoride anion, HF_2^-, by both hexaprotonated ligands and pentaprotonated O-BISTREN, and fluoride ion bridging in the tetra-, penta- and hexaprotonated O-BISTREN. Potentiometric measurements of 1:1 and 1:2 molar ratios of the ligands to Cu(II) in the $NaClO_4$–NaF medium provide equilibrium constants for fluoride ion bridging between the two copper(II) centers in the binuclear cryptate, as well as equilibrium constants for fluoride bridging between copper(II) and protonated nitrogens in the mononuclear copper(II) cryptate. New data for fluoride anion bridging of the protonated species of O-BISTREN and its mononuclear and binuclear copper complexes are reported for 0.10 M ionic strength. The comparison between O-BISTREN and C-BISTREN reveals the high specificity of the binuclear Cu(II)–O-BISTREN cryptate for hydroxide ion bridging.

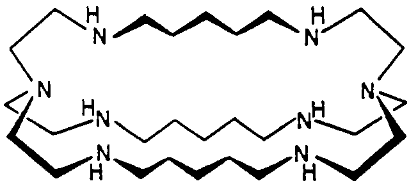
Introduction

The protonation constants and metal ion stability constants of the binucleating cryptand ligand O-BISTREN (7,19,30-trioxa-1,4,10,13,16,22,27,33-octaazabicyclo[11.11.11]pentatriacontane, **1**) have been described in a previous publication.[1] The polyprotonated forms of the ligand as well as its mononuclear and binuclear transition metal ion cryptates were found to strongly bind bridging anions such as hydroxide and chloride ions.[1,2] The unusually high binding constant for hydroxide bridging in the binuclear Cu(II) cryptate was especially noted, and compared with the much lower binding constants for mononuclear Cu(II) complexes with analogous ligands. The unique nature of the hydroxo-bridged binuclear Cu(II)–O-BISTREN cryptate was also illustrated by comparison with the bridging constant of the binuclear Cu(II) cryptate with the isoelectronic fluoride ion, although this comparison was marred somewhat by the fact that the fluoride data were measured at 1.0 M ionic strength.[3] It was suggested[2,3] that the special nature of the hydroxo bridge could be due to stabilization through hydrogen bonding to one or more ether oxygens of the cryptand.



1 (O-BISTREN)

One way of testing these ideas would be to determine analogous binding constants including hydroxide and fluoride bridging constants for a macrobicyclic cryptand having a structure similar to that of O-BISTREN, but without the bridging ether oxygens. This binucleating ligand, C-BISTREN (1,4,10,13,16,22,27,33-octaazabicyclo[11.11.11]pentatriacontane, **2**), has recently become available,[4] and a sample (ca. 100 mg) was provided for potentiometric studies. This paper reports the potentiometric determination of protonation constants, mononuclear and binuclear Cu(II) stability constants, and the corresponding hydroxide and fluoride bridging constants of C-BISTREN. Also, in order to improve the comparisons between the various O-BISTREN and C-BISTREN species described, fluoride ion binding constants for O-BISTREN at 0.10 M ionic strength have been measured and are reported here for the first time.



2 (C-BISTREN)

Experimental Section

Materials. O-BISTREN was synthesized by I.M. by the use of the procedure described previously.[3] C-BISTREN was synthesized by M. W.H. through the use of the procedure previously published (compound 4 in ref 4). A copper(II) perchlorate solution was prepared from reagent grade material and standardized against EDTA by the well-known titration method employing Murexide as indicator. The base employed was carbonate-free 0.100 M NaOH, standardized with potassium acid phthalate. The NaF and $NaClO_4$ employed were both reagent grade, and the latter was dried to constant weight. The water employed as solvent was doubly distilled from dilute $KMnO_4$ solution.

Potentiometric Measurements. The detailed procedures for potentiometric equilibrium measurements have been described elsewhere.[1] The determination of fluoride ion binding constants was carried out by similar procedures at an ionic strength of 0.10 M maintained by a supporting electrolyte consisting of ca. 0.010 M NaF and sufficient $NaClO_4$ to bring the total ionic strength of the electrolyte solution to 0.100 M. Hydrogen ion concentrations were measured with a Corning Model 150 pH Meter, fitted with blue-glass and calomel reference electrodes in which the standard KCl solution was replaced by NaCl solution. The pH meter–electrode system was calibrated to read $-\log [H^+]$ directly (designated

---

* To whom correspondence should be addressed at Texas A&M University.

[†] The cryptand named BISTREN in previous papers is now renamed O-BISTREN (for the five-atom ether oxygen bridges) and the new cryptand described in this paper is named C-BISTREN (for the five-atom carbon bridges).

(1) Motekaitis, R. J.; Martell, A. E.; Lehn, J. M.; Watanabe, E. I. *Inorg. Chem.* **1982**, *21*, 4253.

(2) Motekaitis, R. J.; Martell, A. E.; Dietrich, B.; Lehn, J. M. *Inorg. Chem.* **1984**, *23*, 1588.

(3) Motekaitis, R. J.; Martell, A. E.; Murase, I. *Inorg. Chem.* **1986**, *25*, 938.

(4) Dietrich, B.; Hosseini, M. W.; Lehn, J. M. *Helv. Chim. Acta* **1985**, *68*, 289 and references therein.

0020-1669/88/1327-3630$01.50/0

as p[H]) by titration of dilute standard hydrochloric acid solution at 0.100 M ionic strength with dilute standard NaOH solution. The logarithm of the ion product constant for water (K_w) was found to be 13.78 in 0.100 M $NaClO_4$. The experimental solution (at least 50.00 mL initially) was measured under an inert atmosphere of CO_2-free nitrogen in a standard jacketed titration cell maintained at 25.00 ± 0.05 °C with circulating thermostated water. Fluoride ion binding constants were determined by carrying out the p[H] equilibrium measurement in the presence of a supporting electrolyte consisting of 0.090 M $NaClO_4$ and 0.010 M NaF. Thus the calculations of fluoride binding involve a minor approximation to the effect that the ionic strength of this mixed electrolyte is assumed to be equivalent to the ionic strength of 0.100 M $NaClO_4$.

All of the binding constants determined for C-BISTREN were obtained with two 0.050-g samples of the ligand. Because each experimental solution required 0.05 mmol of ligand, three runs were made on each solution as follows: for the solution containing perchlorate and fluoride, a p[H] profile was determined for the ligand in the absence of metal ion followed by the addition of excess standard perchloric acid to bring the p[H] back down to the original value; 1 equiv of Cu(II) was added to the experimental solution and standard base was then added in increments to determine a second p[H] profile; at the end of this determination standard perchloric acid was again added to bring the p[H] back to the original value, a second equivalent of Cu(II) was added, and a thrid p[H] profile was then measured by adding incremental amounts of standard NaOH. The same procedure was employed for the system containing only perchlorate as supporting electrolyte, thus providing six p[H] profiles from two experimental solutions of the ligand.

An appropriate quantity of $NaClO_4$ was added after each reacidification in order to maintain the ionic strength at μ = 0.1000 M. In order to avoid formation of excessive concentrations of HF, the initial p[H] values were kept at 4.3. The fluoride titrations were carried out with a polyethylene liner fitted snugly within the cell in order to minimize the area of exposed glass.

Computations. The proton association constants and metal ion stability constants were calculated by the Fortran program BEST,[5,6] with the use of the VAX 11/780 computer of the Chemistry Department of Texas A&M University. The distributions of molecular species were computed with a Hewlett Packard Model 150II Microcomputer with the program SPE,[6] written in Fortran 77 based on the algorithm taken from the program BEST. The species diagrams were generated with a Hewlett Packard Laser Jet Plus with software written with Microsoft GW Basic.

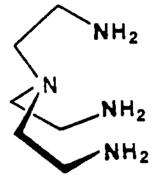
The stepwise microscopic fluoride binding constants were determined from comparisons of the respective overall stability constants measured in the presence and in the absence of fluoride ion through the use of the formula

$$(\beta_F/\beta - 1)/[F^-] = K^x$$

For example if β is given by $[M_2L]/[M]^2[L]$ then the corresponding β_F is $[M_2FL]/[M]^2[F][L]$. Almost identical values for these microscopic constants were obtained from comparisons of overall stability constants calculated for fluoride containing solutions but not involving fluoride ion in the equilibrium expression itself. In this case the effect of fluoride is reflected in the magnitude of the stability constant and can be easily factored out to give essentially the same values for the microscopic constants as above.

Results and Discussion

Protonation Constants. The stepwise protonation constants of O-BISTREN and C-BISTREN are listed in Table I, together with those of the tetradentate ligand TREN (3). These values were computed from potentiometric equilibrium data consisting of profiles of −log [H] vs moles of NaOH added per mole of ligand present. It is seen that both ligands have six successive protonation constants in the presence of perchlorate only, but in the presence of fluoride ion (Table II), there are seven successive protonation constants that require the addition of excess HCl prior to the potentiometric determination of the p[H] profiles. For both



3 (TREN)

Table I. Stepwise Protonation Constants for O-BISTREN, C-BISTREN, and TREN[a]

no.	const O-BISTREN	C-BISTREN	TREN
1	9.99	10.35	10.12
2	9.02	9.88	
3	7.98	8.87	9.41
4	7.20	8.38	
5	6.40	8.14	8.47
6	5.67	7.72	

[a] μ = 0.100 M ($NaClO_4$); T = 25.0 °C.

Table II. Logarithm of the Overall Protonation Constants for O-BISTREN and C-BISTREN[a]

	log (const)		stoichiometry		
no.	O-BISTREN	C-BISTREN	L	F	H
1	9.99	10.35	1	0	1
2	19.01	20.24	1	0	2
3	26.99	29.10	1	0	3
4	34.19	37.48	1	0	4
5	40.59	45.62	1	0	5
6	46.26	53.34	1	0	6
7	36.21		1	1	4
8	44.21		1	1	5
9	50.19		1	1	6
10	56.18	62.04	1	2	7

[a] μ = 0.100 M (0.090 M $NaClO_4$ + 0.010 M NaF); T = 25.0 °C.

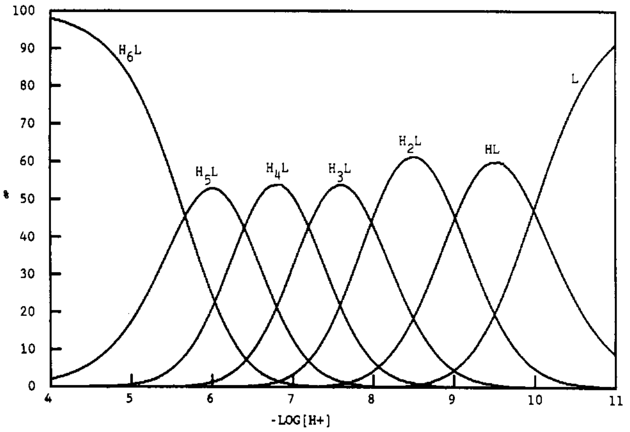


Figure 1. Distribution of species in a solution containing O-BISTREN alone in 0.100 M $NaClO_4$ at 25.0 °C. $T_{O\text{-}BISTREN}$ = 1.000 × 10^{-3} M.

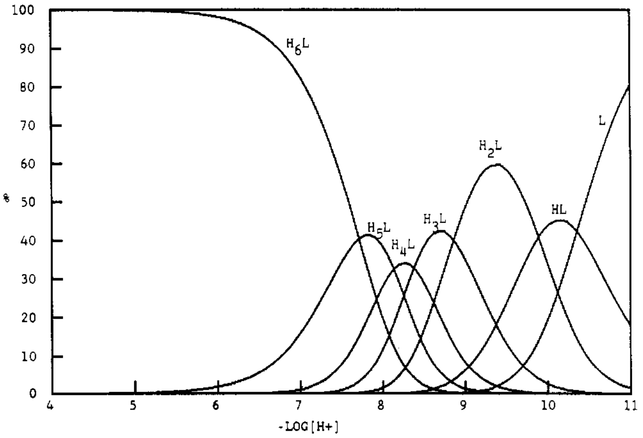


Figure 2. Distribution of species in a solution containing C-BISTREN alone in 0.100 M $NaClO_4$ at 25.0 °C. $T_{C\text{-}BISTREN}$ = 1.000 × 10^{-3} M.

---

(5) Motekaitis, R. J.; Martell, A. E. *Can. J. Chem.* **1982**, *60*, 2403.

(6) Motekaitis, R. J.; Martell, A. E. *New Developments in the Determination and Reporting of Stability Constants*; VCH Publishers: New York, 1988; in press.

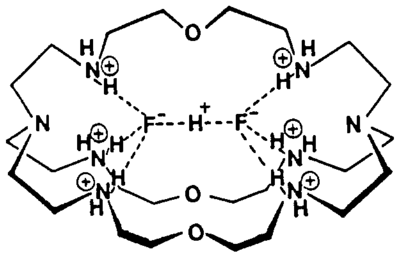
Table III. Fluoride Binding Constants for O-BISTREN and C-BISTREN[a]

quotient Q	log Q	
	O-BISTREN	C-BISTREN
$[H_6LF]/[H_6L][F]$	3.9	
$[H_5LF]/[H_5L][F]$	3.6	
$[H_4LF]/[H_4L][F]$	2.0	
$[H_6LF_2H]/[H_6L][F_2H]$	6.4	5.2
$[H_5LF_2H]/[H_5L][F_2H]$	5.3	

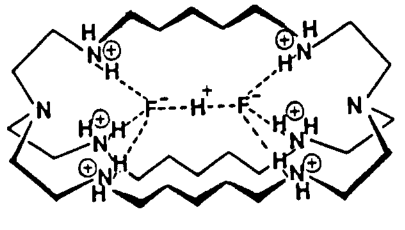
[a] μ = 0.100 M (0.090 M $NaClO_4$ + 0.010 M NaF); T = 25.0 °C.

cryptand ligands the protonation constants are seen to drop steadily as the number of protons on the ligand increase. The decrease in protonation constants is considered to be due to both statistical factors and gradually increasing Coulombic repulsions as the ligand become protonated. The relative values of the protonation constants are illustrated by the species distribution curves for O-BISTREN (Figure 1) and C-BISTREN (Figure 2). In O-BISTREN the spacing of the constants and the curves showing the relative concentrations of the individual protonated species are fairly uniform as the p[H] is increased. In C-BISTREN the spacings are considerably compressed and are less uniform relative to those of O-BISTREN. The differences that are observed are probably due to the complex interplay of statistical factors and Coulombic repulsions of the many individual microscopic species of the partially protonated ligands. A more detailed discussion of the protonation constants of O-BISTREN (**1**) is given elsewhere.[1] Although it is believed that these factors operate in C-BISTREN (**2**) in a manner similar to that of O-BISTREN, it is seen that all of the corresponding protonation constants of the latter are higher than those of O-BISTREN. The lower basicities of the amino nitrogens in O-BISTREN are considered due mainly to the electron-withdrawing ether oxygens in the five-atom bridges between the TREN moieties. The protonation constants of TREN (**3**) are listed in Table I at positions corresponding more or less to equivalent degrees of protonation, compared to O-BISTREN and C-BISTREN. Here it is seen that the amino nitrogens of C-BISTREN are more basic than those of TREN itself, a fact that is ascribed to alkyl substitution on the amino nitrogen and is in accord with the general observation that secondary nitrogens are more basic than primary nitrogens.[7] While this factor seems to operate for the first two protonations of TREN, the situation is reversed for the addition of the last proton to the ligand molecule (the last two for the C-BISTREN ligand). This reversal is considered due to the constraints in the conformation of the TREN units in C-BISTREN (also for O-BISTREN), which results in Coulombic repulsions between the positive protonated amino nitrogens that are much higher than those in the triprotonated TREN ion, for which the protonated nitrogens are able to assume extended conformations in aqueous solution that lessen the Coulombic repulsions between the positively charged protonated nitrogen units.

It is seen from the protonation constants in Table II that when the medium contains a replacement of 10% of the perchlorate by fluoride, higher values of the protonation constants are obtained when the ligand contains more than three positive charges, with the increment increasing rapidly with the charge on the ligand. This increase in protonation constant is considered to be due to fluoride anion binding within the polyprotonated cryptand structure in the manner indicated for anion binding in previous publications.[1-3] The hydrogen bonding that stabilizes the anion complex also stabilizes the hydrogen ions on the protonated secondary amino nitrogens of the cryptand, thus increasing the protonation constant. The seventh protonation reaction of O-BISTREN and C-BISTREN has been found to require a second bound fluoride ion within the crypt and therefore is assigned a position midway between the two fluoride ions, thus making up the HF_2^- unit, which in turn is stabilized and held within the cryptand through hydrogen bonding to the protonated positively charged amino groups, as indicated by formulas **4** and **5**. While the arrangements of hydrogen-bond anions in **4** and **5** seem entirely reasonable, proof for these conformations must await crystal structure studies, and attempts to crystallize these species are now in progress. However, support for representations **4** and **5** comes from the crystal structure of the azide cryptate of hexaprotonated O-BISTREN, in which the linear triatomic species N_3^-, whose overall size is similar to that of the F_2H^-, is indeed held inside the cavity in the manner shown in **4** and **5**. It is noted that the bifluoride binding constant indicated for C-BISTREN in Table III is somewhat lower than that of O-BISTREN. This decrease may be ascribed to the structural difference between O-BISTREN and C-BISTREN. In the latter the most stable conformation of the pentamethylene chain is fully extended, thus increasing the distance between the two TREN subunits in C-BISTREN as compared to O-BISTREN. Furthermore, the pocket containing the bound anions in C-BISTREN is somewhat less hydrated than the corresponding cavity in O-BISTREN thus providing a more hostile environment for the stabilization of the ionic species indicated in formula **5**. These factors would seem to be more important than and would seem to overcome the Coulombic repulsions between the bound anions within the cryptand cavity and the ether oxygens in the five-atom bridges between the TREN units. It is also noted that the fluoride bonding constants of O-BISTREN at an ionic strength of 0.10 M are slightly higher than those reported previously for O-BISTREN.[3] This difference is expected in view of the general effect of ionic strength on complex formation between charged species. When charge neutralization occurs on complex formation, higher ionic strength stabilizes the component ions more than the complex, and decreases in complex formation constants are therefore generally observed as ionic strength increases.



4 ($[H_6L{\cdot}HF_2]^{5+}$) (L = O-BISTREN)



5 ($[H_6L'{\cdot}HF_2]^{5+}$) (L′ = C-BISTREN)

The distribution curves in figure 3 illustrate the extent of fluoride ion binding as a function of p[H] in the case of O-BISTREN. It is seen that the hexaprotonated cryptand ligand is by far the most effective in anion binding, as expected, and binds both the simple fluoride ion (ca. pH 5–8) and, at pH values below 5, the HF_2^- unit. It is suggested that the bifluoride complex, which is assigned the formula H_6LF_2, probably also contains the HF_2^- unit in the center of the cavity, with five protonated amino nitrogens providing the hydrogen bonds necessary to complex this anion. The basis for this suggestion is mainly the fact that a central hydrogen ion between the two negative fluoride ions would seem to be essential to minimize Coulombic repulsions. It is also noted that stabilization of the bifluoride anion in the cavity of the cryptand results in a higher concentration of this complex than the concentration of the free bifluoride ion in solution.

Copper(II) Complexes of O-BISTREN and C-BISTREN. It has been noted previously that the mononuclear copper(II) binding constant for O-BISTREN (log value 17.59 in Table IV) is sig-

---

[7] Hancock, R. D.; Martell, A. E. *Comments Inorg. Chem.* **1988**, *6*, 237.

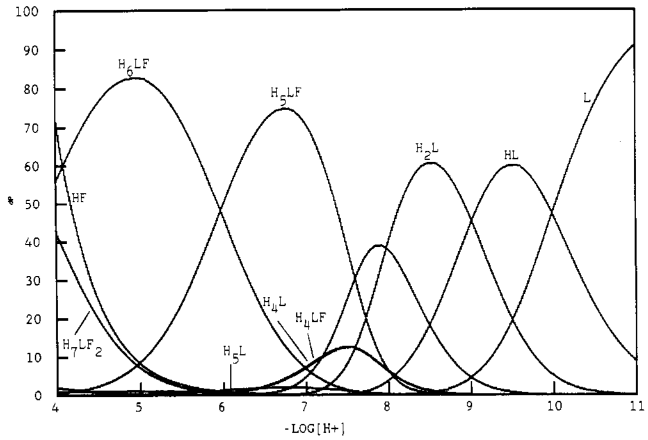


Figure 3. Distribution of species in a solution containing O-BISTREN and fluoride in 0.090 M $NaClO_4$ and 0.010 M NaF. $T_{O\text{-BISTREN}} = 1.000 \times 10^{-3}$ M.

Table IV. Stability Constants for Copper(II)–O-BISTREN and Copper(II)–C-BISTREN Complexes[a]

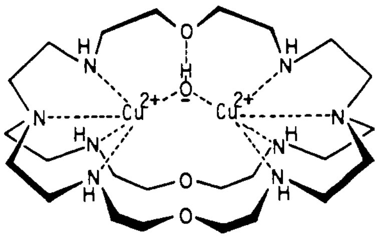
	log Q	
quotient Q	O-BIS-TREN	C-BIS-TREN
$K_{ML} = [ML]/[M][L]$	17.59	15.39
$K^{H}_{MHL} = [MHL]/[ML][H]$	7.92	10.08
$K^{H}_{MH_2L} = [MH_2L]/[MHL][H]$	7.14	8.70
$K^{H}_{MH_3L} = [MH_3L]/[MH_2L][H]$	5.20	7.62
$K^{M}_{M_2L} = [M_2L]/[ML][M]$	10.73	13.37
$K^{-H}_{M_2(OH)L} = [M_2OHL][H]/[M_2L]$	−3.89	−7.59
$K^{-H}_{M_2(OH)_2L} = [M_2(OH)_2L][H]/[M_2OHL]$		−10.81
$K^{H}_{M_2HL} = [M_2HL]/[M_2L][H]$		5.40

[a] μ = 0.100 M ($NaClO_4$); T = 25.0 °C.

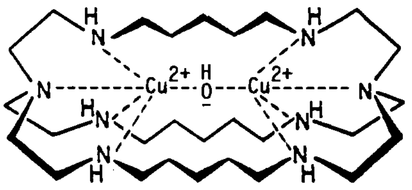
nificantly lower than the corresponding binding constant of copper(II) with the simple chelating ligand TREN itself, and this has been ascribed as being due to the electron-withdrawing effect of the ether oxygens in O-BISTREN.[1] The stability constant data in Table IV indicate that the binding constant of the first copper ion for C-BISTREN is a full 2 log units lower than that of O-BISTREN itself in spite of the fact that it has already been shown above that the amino nitrogens of C-BISTREN are more basic than those of O-BISTREN and hence would be expected to show a higher metal ion affinity. This difference is considered to be due to a greater amount of preorganization of the donor groups of O-BISTREN[7] compared to that of C-BISTREN in which the connecting chains of five carbon atoms in aqueous solution are probably collapsed so that they are close together, thus squeezing out water of solvation and eliminating much of the cavity in the free cryptand ligand. The breaking up of this structure to make room for the first copper(II) ion would be expected to cost considerable energy and result in a lower formation constant. This interpretation is reinforced by the fact that the binding constant for the second copper ion of C-BISTREN is much higher than that for the second metal ion of O-BISTREN (ca. 3.4 log units). Apparently the first metal ion to enter the cavity must spread the hydrocarbon chains, enlarging the cavity and improving the degree of preorganization, thereby making this factor less important when the second metal ion is added to the cryptate complex. Thus one would expect the greater basicity of C-BISTREN amino nitrogens to have a greater stabilizing effect for the second copper ion than the residual destabilizing effect resulting from the remaining lack of preorganization, if any, of the cryptand ligand. Accordingly the overall β value for the binuclear C-BISTREN cryptate (log value 28.3) is somewhat greater than that of O-BISTREN with a log β of 27.4. It is suggested that the difference would be much greater if it were not for the lack of preorganization of the C-BISTREN free ligand.

It is noted from the equilibrium constants listed in Table IV that the successive protonation constants of the mononuclear C-BISTREN cryptate are significantly higher than the corresponding values of the copper(II) O-BISTREN cryptate itself, again a reflection of the greater basicities of the amino groups in C-BISTREN. The mono-, di-, and triprotonated forms of the mononuclear O-BISTREN copper(II) cryptate have been discribed in detail elsewhere.[1,2] On the basis of comparable protonation constants for the corresponding mononuclear C-BISTREN chelate, it is suggested that the conformations of the latter are similar to those of the corresponding O-BISTREN species with the copper ion coordinated at one end of the cryptate cavity and the protonation reactions occurring at the other end, the main difference being the greater basicities of the amino donor groups in C-BISTREN.

The greatest difference in the chemical behavior of O-BISTREN and C-BISTREN can be seen in the hydroxide ion binding constants for the binuclear copper cryptate complexes. The log value of 10.0 for O-BISTREN has been stated previously to be unusually high, as indicated in the Introduction. The hydroxide binding constant of the binuclear C-BISTREN copper cryptate, with a log value of 6.2, is about 4 orders of magnitude weaker than that of O-BISTREN and is probably a more reasonable value for a bridging hydroxide between two closely spaced copper(II) ions. In the search for a reason for the high binding constant of binuclear copper O-BISTREN it was suggested that the bridging hydroxide is further stabilized by hydrogen bonding to one of the bridging ether oxygens as indicated by **6**.[1] In the case of the corresponding C-BISTREN complex, **7**, there are no ether oxygens, and such additional stabilization of the bridging hydroxide ion is not possible. The significantly lower binding constant of the latter may be taken as further support for the suggestion of hydrogen bonding in **6**. Furthermore, because of the more extended shape of C-BISTREN (vide supra) the distance of the two copper(II) ions in its dinuclar complex should be longer than in the complex of O-BISTREN.



6 ($[Cu_2(OH)L]^{3+}$) (L = O-BISTREN)



7 ($[Cu_2(OH)L']^{3+}$) (L′ = C-BISTREN)

The strong binding constant of the bridging hydroxide ion provides a high degree of stabilization of the binuclear copper O-BISTREN cryptate. The distribution curves for the 2:1 Cu(II)–O-BISTREN system illustrated in Figure 4 show the predominance of the hydroxide-bridged binuclear chelate over most of the other species. The only other complex formed to any extent is the triprotonated mononuclear copper(II) O-BISTREN complex between pH 3.5 and 4.5. The so-called "normal" binuclear cryptate, M_2L^{4+}, is only a minor species formed to the extent of 19%. For that reason calculation of its stability constant somewhat less accurate, and it is listed in Table IV to one significant figure only. The species distribution curves illustrated in Figure 5 for the 2:1 Cu(II)–C-BISTREN system shows that in this case the situation is entirely different. Here the lower binding constant of the bridging hydroxide ion is reflected by a delay in its formation in appreciable concentrations until the pH is raised to values above 7, beyond which it becomes the major species in solution. At lower pH however, the unhydrolyzed binuclear cryptate complex M_2L

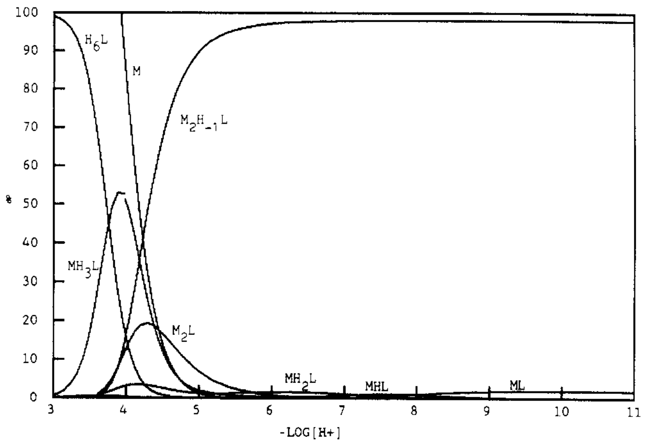


Figure 4. Distribution of species in a solution containing a 2:1 molar ratio of Cu(II) to O-BISTREN in 0.100 M $NaClO_4$ at 25 °C. $T_{\text{O-BISTREN}} = {}^1/_2T_{Cu^{2+}} = 1.000 \times 10^{-3}$ M.

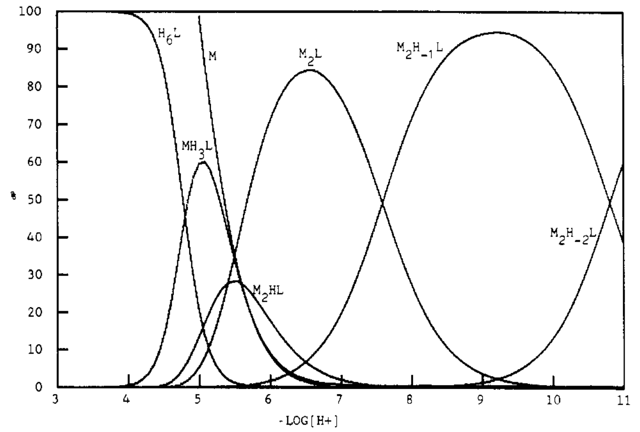


Figure 5. Distribution of species in a solution containing a 2:1 molar ratio of Cu(II) to C-BISTREN in 0.100 M $NaClO_4$ at 25 °C. $T_{\text{C-BISTREN}} = {}^1/_2T_{Cu^{2+}} = 1.000 \times 10^{-3}$ M.

and the mononuclear triprotonated complex are important species in solution. At this point no explanation is offered for the existence of M_2HL, because of the lack of a suggestion as to where the complex may be protonated.

The strong stabilizing effect of the hydroxide ion bridge in the binuclear O-BISTREN–copper(II) cryptate is manifested by the unusual distribution of species in the 1:1 Cu(II)–O-BISTREN system illustrated in Figure 6. Here, in spite of the unfavorable ratio of components, the binuclear hydroxide-bridged Cu(II) cryptate dominates the system from pH 4.5–11. The species distribution diagram is greatly complicated by the release of uncomplexed ligand, which exists in six forms having varying degrees of protonation. The only mononuclear species of any importance are those at nearly neutral and weakly acid conditions, where they are stabilized in the form of their mono-, di-, and triprotonated forms. If one now turns to the corresponding C-BISTREN system (1:1 ligand:copper ratio) for which the hydroxo-bridging binding constant is much lower, the species diagram illustrated in Figure 7 appears to be much closer to what one would expect for a mononuclear complex system. Here the mononuclear complexes stabilized by protonation dominate over most of the pH range with the hydroxo-bridged binuclear complex becoming the major species near pH 10. The less stable binuclear cryptate, M_2L^{4+}, is a relatively minor species accounting for around 23% of the metal ion in the pH range 6–7.

With reference to Table III again, it is noted that the mononuclear Cu(II)–O-BISTREN cryptate hydrolyzes at an unusually high pH, with a hydroxide binding constant of approximately $10^{3.2}$ while the corresponding constant for the mononuclear C-BISTREN cryptate, not listed, may be even somewhat lower (i.e., hydrolysis occurs at a still higher p[H]). The reluctance of the

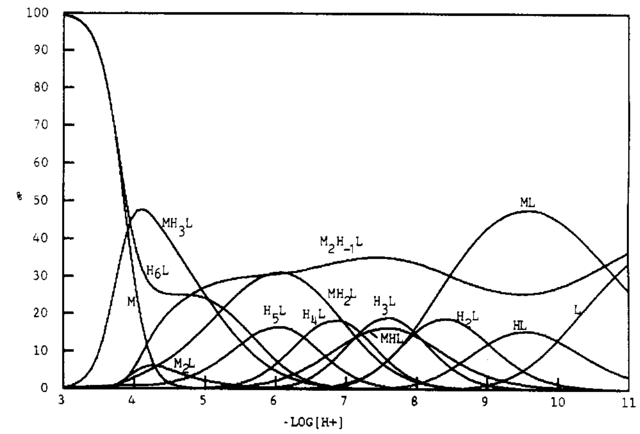


Figure 6. Distribution of species in a solution containing a 1:1 molar ratio of Cu(II) to O-BISTREN in 0.100 M $NaClO_4$ at 25 °C. $T_{\text{O-BSITREN}} = T_{Cu^{2+}} = 1.000 \times 10^{-3}$ M.

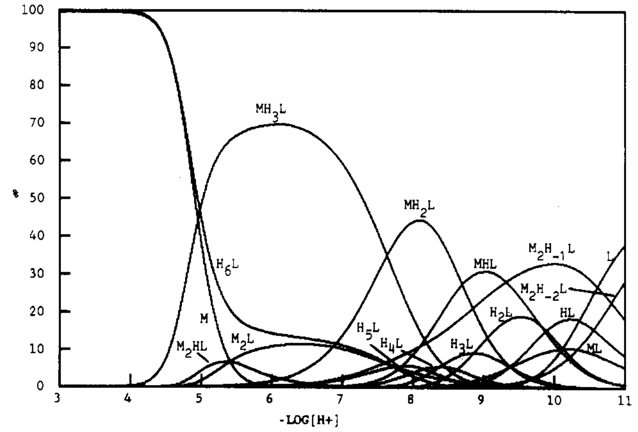
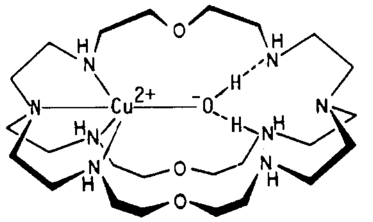
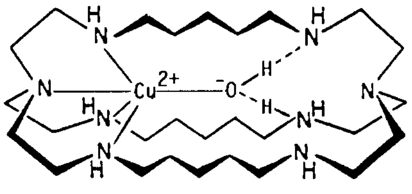


Figure 7. Distribution of species in a solution containing a 1:1 molar ratio of Cu(II) to C-BISTREN in 0.100 M $NaClO_4$ at 25 °C. $T_{\text{C-BISTREN}} = T_{Cu^{2+}} = 1.000 \times 10^{-3}$ M.

mononuclear cryptate to hydrolyze has been used as the basis for suggesting a hydroxo-bridged hydrogen-bonded structure as the species occupying the cavity in the cryptate complex, illustrated by **8**. It is suggested that a similar arrangement exists in the cavity of the mononuclear C-BISTREN–copper(II) cryptate, as indicated by **9**. Thus the reluctance to hydrolyze is suggested as being due to the fact that the metal ion is already hydrolyzed, and the somewhat inhibited hydrolysis step is not favored except at higher pH because it is actually a proton dissociation reaction and would require the removal of a stabilizing hydrogen bond. The existence of a dihydroxo binuclear copper(II)–C-BISTREN cryptate com-

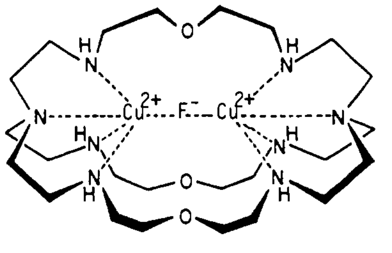


8 ($[Cu(OH)HL]^{2+}$) (L = O-BISTREN)

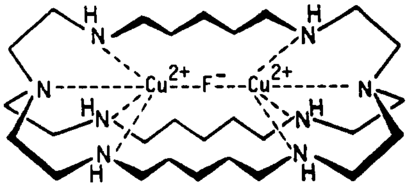


9 ($[Cu(OH)HL']^{2+}$) (L′ = C-BISTREN) plex, where such a species has not been detected in the case of the analogous O-BISTREN system, may be a reflection of the fact that dihydrogen complex formation would require a breakup of the hydrogen-bonding arrangement in **6** with the formation of a completely different structure whereas this would not be necessary in **7**. The question as to whether the dihydroxo species would be a dibridged species cannot be settled without further structural information.

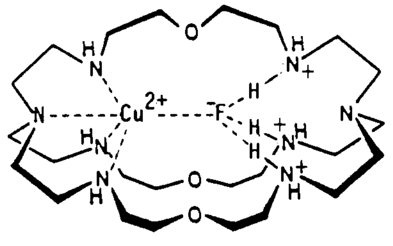
Fluoride Ion Bridging. The fluoride ion binding constants for the Cu(II) cryptate complexes of O-BISTREN and C-BISTREN are listed in Table V. The fluoride-bridged complexes for both the binuclear and mononuclear complexes are represented by formulas **10–13**. The data show that the fluoride bridging constants for the O-BISTREN and C-BISTREN systems differ by a factor of approximately $10^{1.4}$. This, compared to a 10^4 factor for the corresponding hydroxo bridge complexes, lends further support to the unique nature of the monohydroxo-bridged binuclear copper(II)–O-BISTREN cryptate complex, **6**. The lower binding constant of the fluoride ion for the binuclear copper(II)–C-BISTREN cryptate may be rationalized on the basis of the higher stability of the C-BISTREN–copper(II) complex, due to the stronger Cu(II)–amino nitrogen coordinate bonds of C-BISTREN. The greater basicities of the donor nitrogens in C-BISTREN have been discussed above. It is well-known that high affinity of a primary ligand for a metal ion tends to decrease the affinity of that metal ion for a secondary ligand. Thus the greater intrinsic coordinate bond strength between the copper(II) and the basic nitrogens of C-BISTREN would lead one to expect a lower fluoride ion binding affinity relative to the corresponding reactions in the O-BISTREN cryptates, as is observed. Values for the fluoride ion binding to the mono-, di-, and triprotonated mononuclear copper(II)–O-BISTREN and copper(II)–C-BISTREN cryptates seem to be quite similar, with the values for C-BISTREN being somehwat lower. These differences may again be rationalized on the basis of the greater basicities of the amino nitrogens of C-BISTREN relative to those of O-BISTREN.



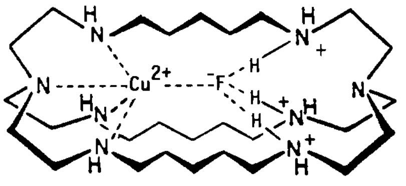
10 ($[Cu_2LF]^{3+}$) (L = O-BISTREN)



11 ($[Cu_2L'F]^{3+}$) (L′ = C-BISTREN)



12 (mononuclear F^- O-BISTREN)



13 (mononuclear F^- C-BISTREN)

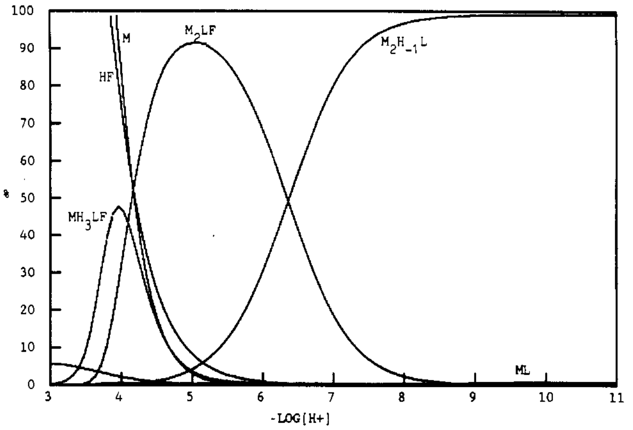


Figure 8. Distribution of species in a solution containing a 2:1 molar ratio of Cu(II) to O-BISTREN in 0.090 M $NaClO_4$ and 0.010 M NaF. $T_{\text{O-BISTREN}} = {}^1/_2T_{\text{Cu}^{2+}} = 1.000 \times 10^{-3}$ M.

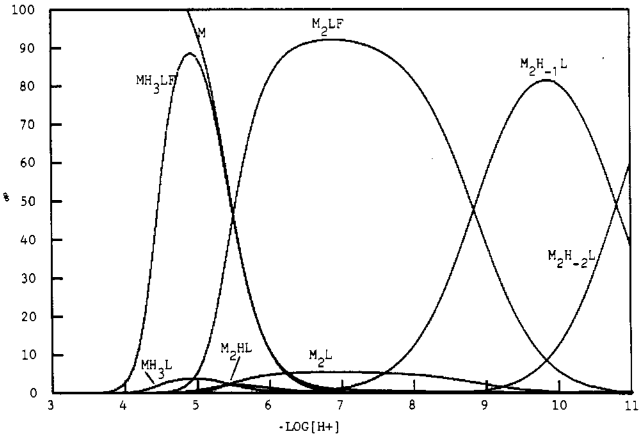


Figure 9. Distribution of species in a solution containing a 2:1 molar ratio of Cu(II) to C-BISTREN in 0.090 M $NaClO_4$ and 0.010 M NaF. $T_{\text{C-BISTREN}} = {}^1/_2T_{\text{Cu}^{2+}} = 1.000 \times 10^{-3}$ M.

The fluoride ion binding constants in Table V may be used to calculate the species distributions in 2:1 Cu(II)–ligand systems and 1:1 ligand–Cu(II) solutions for O-BISTREN and C-BISTREN. The distribution diagrams illustrated in Figures 8–11 provide interesting comparisons with the corresponding diagrams in Figures 4–7 indicating the competition between fluoride and hydroxide ion for bridging the two copper ions in the cryptate cavity or bridging one copper ion and the positive protonated amino groups. Figure 8 shows that fluoride competes well with hydroxide for bridging the two Cu(II) centers in the binuclear O-BISTREN chelate but only between pH 4 and 6 where the free hydroxide ion concentration is estremely low. Thus the much more strongly bound hydroxide ion dominates the system above p[H] 6 and the hydroxo-bridged species is virtually the only complex present above p[H] 8. Because of the lower hydroxide ion binding constant for C-BISTREN (Figure 9), fluoride bridging predominates over hydroxide bridging over a wide p[H] range, ca. 5–8.5, while hydroxo-bridged species dominate above p[H] 9, eventually giving way to a dihydroxo species. Thus it is seen that fluoride ion stabilizes the unhydrolyzed binuclear cryptate complex to form M_2LF, **10**, by fluoride bridging because of lowered competition from hydroxide bridging. Similar stabilization is seen in Figure 10 by the fluoride ion of the triprotonated mononuclear cryptate, which in this case becomes a major species between p[H] 4 and 5.5.

For the 1:1 metal–ligand systems (Figures 6 and 7), it was noted that for the fluoride-free complexes the hydroxo-bridged binuclear

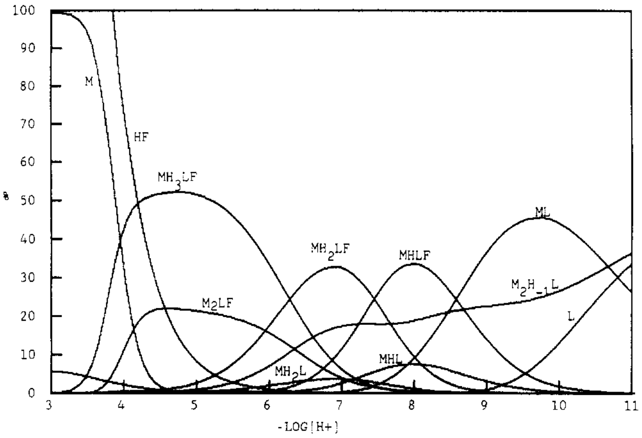


Figure 10. Distribution of species in a solution containing a 1:1 molar ratio of Cu(II) to O-BISTREN in 0.090 M $NaClO_4$ and 0.010 M NaF. $T_{O\text{-BISTREN}} = T_{Cu^{2+}} = 1.000 \times 10^{-3}$ M.

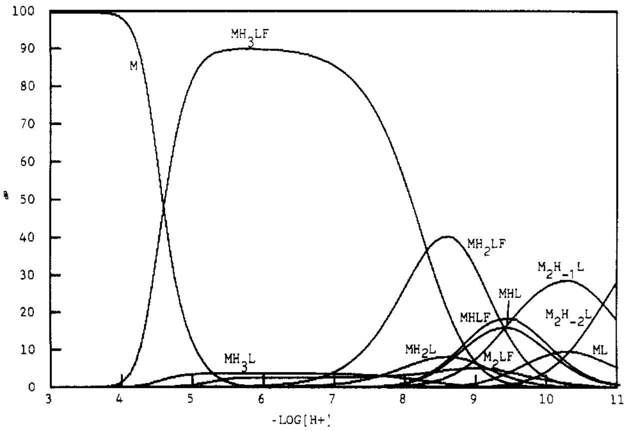


Figure 11. Distribution of species in a solution containing a 1:1 molar ratio of Cu(II) to C-BISTREN in 0.090 M $NaClO_4$ and 0.010 M NaF. $T_{C\text{-BISTREN}} = T_{Cu^{2+}} = 1.000 \times 10^{-3}$ M.

complex dominates solutions made up with 1:1 ligand-metal ion stoichiometry. As seen in Figure 10 the addition of fluoride does not greatly alter that situation, and binuclear complexes dominate the solution from p[H] 4.5-12, even though the ratio of ligand to metal present is 1:1. The main difference in the two systems is that fluoride bridging seems to compete with hydroxide bridging in the low p[H] range, 4.5-6, under which conditions the free hydroxide ion concentration in solution is extremely low. In the case of C-BISTREN (Figure 11), the situation is quite different, and mononuclear complexes, stabilized by fluoride, dominate the system from p[H] 4.5 to 10. The fluoride-bridged triprotonated mononuclear cryptate complex of C-BISTREN seems to be especially stable and is the major species in solution to the exclusion of most others from p[H] 4.5 to 8.5, above which it undergoes successive deprotonation. Finally at p[H] 9.5 the hydroxo-bridged binuclear cryptates become the major species, increasing from 70% of the metal ion at that point to 100% at very high p[H].

Table V. Fluoride Binding Constants for Copper(II) Complexes of O-BISTREN and C-BISTREN

	log *Q*	
quotient *Q*	O-BISTREN	C-BISTREN
$[M_2LF]/[M_2L][F]$	4.5	3.3
$[MH_3LF]/[MH_3L][F]$	4.1	3.4
$[MH_2LF]/[MH_2L][F]$	3.0	2.7
$[MHLF]/[MHL][F]$	2.7	2.1

[a] $\mu = 0.100$ M (0.090 M $NaClO_4$ + 0.010 M NaF); $T = 25.0$ °C.

Conclusions

This potentiometric study has provided a description of the complex species formed as a function of p[H] by the cryptand ligands O-BISTREN and C-BISTREN in the presence of and in the absence of copper(II) ions and in the presence and in the absence of fluoride ion. The results provide new insights into the nature of hydroxide bridging in the binuclear copper(II)-O-BISTREN cryptate by showing the behavior in the corresponding binuclear copper(II)-C-BISTREN cryptate. The special nature of hydroxide bridging in the binuclear copper(II)-O-BISTREN cryptate and the hydrogen-bonded structure suggested for it in this paper are further supported by the information provided on fluoride ion bridging in these two binuclear cryptate system, whereby it was found that the strength of fluoride ion bridging is very similar for the two binuclear cryptates.

Acknowledgment. This research was supported by a grant, No. A-259, from The Robert A. Welch Foundation.

Registry No. 1, 64819-97-2; 2, 99269-13-3; F^-, 16984-48-8; OH^-, 14280-30-9; HF_2^-, 18130-74-0.

Contribution from the Department of Chemistry,
Texas A&M University, College Station, Texas 77843

Synthesis and Characterization of $[Et_4N][M(CO)_5SR]$ and $[Et_4N]_2[M_2(CO)_8(SR)_2]$ Complexes (M = Cr, Mo, W). Ligand Substitution Reactions and X-ray Crystal Structure of $[Et_4N]_2[W_2(CO)_8(SPh)_2]$

Donald J. Darensbourg,* Kathryn M. Sanchez, and Joe Reibenspies

Received March 4, 1988

A series of complexes, $[Et_4N][M(CO)_5SR]$ (M = Cr, Mo, W; R = H, Ph), have been synthesized and characterized by ^1H and ^{13}C NMR and IR spectroscopies. Gentle heating causes these complexes to lose a carbonyl ligand, yielding the doubly bridged sulfur dimers $M_2(CO)_8(\mu\text{-}SR)_2^{2-}$. The X-ray crystal structure of $[Et_4N]_2[W_2(CO)_8(SPh)_2]$ has been determined. The complex crystallizes in the triclinic space group $P\bar{1}$ with unit cell parameters $a = 9.8664$ (17) Å, $b = 9.8566$ (22) Å, $c = 11.8270$ (26) Å, $\alpha = 65.790$ (16)°, $\beta = 81.710$ (16)°, $\gamma = 82.000$ (16)°, $V = 1034.0$ (4) Å^3, and $Z = 1$. Both mono- and dinuclear metal complexes readily react with phosphorus donor ligands to afford the carbon monoxide substituted complexes *cis*-$M(CO)_4(P)(SR)^-$ (P = PMe_3, $P(OMe)_3$, PPh_3). In addition, the dimers react with 1 atm of carbon monoxide to re-form the mononuclear species $M(CO)_5SR^-$ in quantitative yields. Unsuccessful attempts to insert CO_2, COS, or CS_2 into the M-SR bond in the $M(CO)_5SR^-$ derivatives are noted.

Introduction

The chemistry of metal sulfur complexes has been receiving an increasing amount of attention in recent years. There has been tremendous interest in the synthesis of complexes that model the environment about the transition-metal centers in a number of biologically important enzymes. The structure of the FeMo-co-

0020-1669/88/1327-3636$01.50/0