negative than the anodic limit of our solvent. These studies are presently under way.

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Bis-tren Cryptates of Cobalt(II), Nickel(II), Copper(II), and Zinc(II). Protonation Constants, Formation Constants, and Hydroxo Bridging

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Potentiometric equilibrium measurements of hydrogen ion concentration have been employed for the determination of protonation constants of the macrobicyclic ligand bis-tren at 25 °C in solutions maintained at 0.10 M ionic strength with potassium nitrate, sodium perchlorate, potassium chloride, and the sodium salt of 2,4,6-trimethylbenzenesulfonic acid as supporting electrolytes. The protonation constants were found to be dependent on the nature of the supporting electrolyte, with sodium perchlorate and sodium trimethylbenzenesulfonate having considerably less interaction with the ligand than potassium nitrate and potassium chloride. These results are interpreted in terms of nitrate and chloride binding to the protonated ligand. With the divalent metal ions, bis-tren forms in each case mononuclear and dinuclear inclusion complexes of the cryptate type, as well as a series of protonated and hydroxo derivatives. The mononuclear complexes are less stable than those of tren itself and yield protonated forms. The binding of the second cation is weaker than that of the first. It gives dinuclear cryptates which further take up anions, forming cascade type complexes. Thus, the cryptate structure stabilizes bridging of the two bound metal ions by one or two hydroxo groups. The dinuclear Co(II) complex was found to combine reversibly with dioxygen, forming a doubly bridged species containing both hydroxo and peroxo bridges within the cryptate structure.

Introduction

Macropolycyclic ligands containing two binding subunits are able to form dinuclear cryptates by inclusion of two metal cations into the molecular cavity and may further bind substrate species held by the cation centers, yielding cascade complexes.[2] Such is the case, in particular, with the bis-tren cryptand **1**, a macrobicyclic system that was found to complex
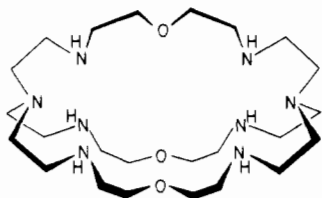
1, schematic representation of bis-tren free base

two cations by its two tren (2,2′,2″-triaminotriethylamine) type subunits, forming dinuclear cation cryptates of the axial macrobicyclic type.[2a] The synthesis of **1** and its complexation with a number of transition-metal cations have been reported earlier.[2b] The hexaprotonated form of bis-tren was found to bind selectively a number of anions presumably by hydrogen bonding with the protonated nitrogen sites and inclusion into the molecular cavity, yielding anion cryptates.[3] We now report potentiometric studies on the formation of mono- and dinuclear cryptates between **1** and Co(II), Ni(II), Cu(II), and Zn(II) cations, as well as bridged cascade type species.

Experimental Section

Materials. Bis-tren (7,19,30-trioxa-1,4,10,13,16,22,27,33-octaa-zabicyclo[11.11.11]pentatriacontane) was synthesized by the method previously described.[2b] In this work two samples were employed, a 0.10-g sample of the crystalline perchlorate and a 0.100-g sample of the free base. Since the latter is hygroscopic, the stock solution required standardization by potentiometric titration. Stock solutions (0.0200 M) of reagent grade metal nitrates were prepared in doubly distilled water, and their exact concentrations were determined by direct potentiometric titration with standard EDTA[4] in the presence of appropriate indicators. A carbonate-free solution of 0.1000 M potassium hydroxide was prepared from Dilut-it ampules and standardized with potassium acid phthalate. The supporting electrolytes potassium nitrate, potassium chloride, and sodium perchlorate were also obtained as reagent grade materials. The sample of tren employed for comparison with bis-tren was commercial grade material that was further purified by fractional distillation and successive recrystallizations from hydrochloric acid. The sodium 2,4,6-trimethylbenzenesulfonate used as a supporting electrolyte was prepared by sulfonation of 1,3,5-trimethylbenzene and was purified by successive recrystallizations from water–ethanol mixtures.

Procedures. The potentiometric equilibrium measurements of tren and bis-tren in the absence and in the presence of metal ions were carried out with a Beckman Research pH meter fitted with blue-glass and calomel reference electrodes and calibrated to read −log [H$^+$] directly. The temperature was maintained at 25.00 ± 0.05 °C, and the ionic strength was adjusted to 0.100 M by the addition of the

(1) (a) Texas A&M University. (b) Université Louis Pasteur.
(2) (a) Lehn, J. M. *Pure Appl. Chem.* **1980**, *52*, 2441. (b) Lehn, J. M.; Pine, S. H.; Watanabe, E. I.; Willard, A. K. *J. Am. Chem. Soc.* **1977**, *99*, 6766.
(3) Lehn, J. M.; Sonveaux, E.; Willard, A. K. *J. Am. Chem. Soc.* **1978**, *100*, 4914. Lehn, J. M.; Sonveaux, E., unpublished results.

(4) Welcher, R. J.; Johnson, F. "The Analytical Uses of Ethylenedi-aminetetraacetic Acid"; Van Nostrand-Reinhold: Princeton, NJ, 1958.
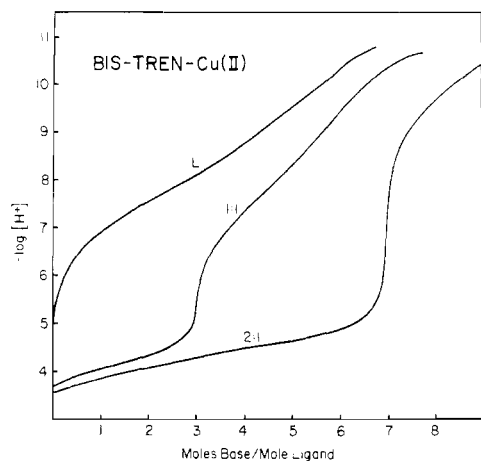
Figure 1. Potentiometric equilibrium data for bis-tren (1) and its Cu(II) complexes: (L) the bis-tren hexahydroperchlorate; (1:1) 1:1 molar ratio of Cu(II) to bis-tren·6HClO$_4$; (2:1) 2:1 molar ratio of Cu(II) to bis-tren·6HClO$_4$.

appropriate supporting electrolyte. Typical concentrations of experimental solutions were 0.00100 M in ligand with molar concentrations of metal ion equivalent to that of the ligand or twice that of the ligand. Oxygen and carbon dioxide were excluded from the reaction mixture by maintaining a slight positive pressure of purified nitrogen in the reaction cell. The nitrogen was replaced by pure oxygen for the potentiometric work involving dioxygen complex formation in the Co(II) system.

Computations. The proton association constants of tren and bis-tren were calculated with the program PKAS,[5] with the aid of a CDC 1604A computer, and a Micromation 64K microcomputer equipped with dual disk drives. Formation constants of the 1:1 and 2:1 metal–ligand complexes were obtained algebraically with the use of appropriate mass-balance and charge-balance equations evaluated at each equilibrium point of the potentiometric equilibrium curves. Refinement of the preliminary values thus obtained was carried out with the program BEST, written in these laboratories.[6] In this program the input consists of the components and their concentrations, the initial values of the equilibrium constants for each species considered to be present, and the potentiometric equilibrium data determined experimentally. The program sets up simultaneous mass-balance equations for all components at each neutralization value involving the concentration of base added to the experimental solution and solves for the concentration of each species present. Equilibrium constants are then varied in order to minimize the differences between the calculated and observed values of $-\log$ [H$^+$]. The species considered present in the experimental solutions are those that one would expect to form according to established principles of coordination chemistry including protonated metal chelates and hydroxometal chelate species. Care was taken not to "invent" additional complex species merely for the purpose of improving the fit of the calculated results to the experimental curves. The errors reported are based on the differences between the calculated and experimental hydrogen ion concentrations over the entire equilibrium curve for each system.

Potentiometric Data. Sample experimental potentiometric data are illustrated in Figure 1, which shows potentiometric equilibrium curves for the hexahydroperchlorate of bis-tren, a 1:1 molar ratio of the hexaperchlorate of bis-tren and copper(II) ion, and a 1:2 molar ratio of the hexaperchlorate of bis-tren and copper(II) ion. The free-ligand curve has a long sloping buffer region with no apparent breaks for the six protonation steps. For the formation of the mononuclear Cu(II) cryptate it is seen that three protons are neutralized at low pH as the metal becomes coordinated to give a triprotonated cryptate chelate. At higher pH there is a long buffer region corresponding to overlapping neutralization steps for the three protons coordinated to the other half of the bis-tren ligand. There is no break in the curve at high pH because of the formation of a monohydroxo cryptate species and eventually the presence of appreciable free hydroxide ion in solution. For the dinuclear cryptate it is seen that seven

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Table I. log (protonation constants) of tren in Various Media[a]

KCl	KNO$_3$	(CH$_3$)$_3$PhSO$_3$Na	NaClO$_4$
10.17	10.15	10.18	10.12
9.47	9.45	9.46	9.41
8.43	8.43	8.39	8.42

[a] t = 25.00 °C; μ = 0.100.

Table II. Successive log (protonation constants) of Bis-tren in Various Supporting Electrolytes[a,b]

KCl	KNO$_3$	(CH$_3$)$_3$-PhSO$_3$Na	NaClO$_4$	log (nitrate binding const)[c]	log (chloride binding const)
9.89	9.93	9.92	9.89		
9.17	9.31	9.26	9 23	0.50	
8.26	8.55	8.22	8.29	1.15	
7.89	7.91	7.53	7.65	1.52	0.62
7.28	7.32	6.68	6.64	2.30	1.71
6.60	6.63	6.05	6.01	2.93	2.26

[a] t = 25.00 °C; μ = 0.100. [b] The standard deviations in log [H$^+$] range from 0.0008 to 0.0024 log unit. [c] Relative to the binding constant with 0.100 M perchlorate as supporting electrolyte.

protons are neutralized at low pH, indicating a strong tendency to form the monohydroxo-bridged binuclear copper(II) cryptate. A second hydrolysis step is also seen at high pH, resulting in the formation of the dihydroxo-bridged dinuclear copper(II) cryptate.

Results and Discussion

Proton and Anion Binding. The proton association constants of tren and bis-tren in four supporting electrolytes are presented in Tables I and II, respectively. No significant variation in the equilibrium constants of tren was observed for the supporting electrolytes investigated. In the case of bis-tren, considerable variation in protonation equilibria was apparent when potassium nitrate and potassium chloride were used to control the ionic media, relative to that for the solutions in which the ionic strengths were controlled by sodium trimethylbenzenesulfonate and sodium perchlorate. The lower protonation constants of bis-tren were significantly higher in nitrate and chloride media than in perchlorate and trimethylbenzenesulfonate, indicating higher anion binding in solutions containing the former supporting electrolytes. The fact that the pK's were not significantly different in trimethylbenzenesulfonate and perchlorate media does not necessarily mean that anion binding is nonexistent in these media, but it does mean that the binding constants would be at least considerably lower and approximately equivalent. In fact weak binding by perchlorate at the level of log $K \lesssim 1$ has been noted previously.[3]

The weakness of interaction with perchlorate makes possible the use of sodium perchlorate as a reference supporting electrolyte and thus the calculation of nitrate and chloride binding constants (relative to those for perchlorate binding) from differences in protonation constants. Thus for the purpose of calculating apparent binding constants, the protonation constants listed in Table II for perchlorate media were assumed to involve no interference by the supporting electrolyte. The pK's of bis-tren species containing 6–3 protons are significantly higher in nitrate and chloride than in perchlorate media. Since the hexaprotonated form H$_6$L^{6+} has been shown previously to bind several anions,[3] higher pH values may be assumed to result from stronger binding of the protons involved in the ligand anion complexes. On this basis, nitrate binding constants of bis-tren were calculated to be log K_s = 0.50, 1.15, 1.52, 2.30, and 2.93 for the protonated forms of bis-tren bearing 2, 3, 4, 5, and 6 protons, respectively. The latter value is in good agreement with that determined earlier by other methods.[3] The data indicate that at least two protons

Table III. Formation Constants of Metal Chelates of Bis-tren and tren[a]

	Cu(II)		Ni(II)		Co(II)		Zn(II)	
equil quotient	BT	tren	BT	tren	BT	tren	BT	tren
[ML]/([M][L])	16.54	18.5	11.70	14.6	11.20	12.7	11.86	14.5
[M$_2$L]/([M]^2[L])	29.21		~18.5		16.80		18.22	
([MLOH][H$^+$])/[ML]	−10.23	−9.17	−10.3	−9.8	−9.13	−9.9	−11.1	
([M$_2$LOH][H$^+$])/[M$_2$L]	−4.26		~−6.0		~−7.20		−6.00	
[MHL]/([ML][H$^+$])	8.78		8.72		8.52		8.47	
[MH$_2$L]/([MHL][H$^+$])	7.70		7.76		7.16		7.72	
[MH$_3$L]/([MH$_2$L][H$^+$])	6.87		5.45		6.85		7.03	
[MH$_3$L]/([M][L][H$^+$]^3)	39.89		33.63		33.73		35.08	

[a] At 25.00 °C and $\mu = 0.100$ M. log ([Co$_2$L(OH)O$_2$]/([Co$_2$L(OH)]P_{O_2})) = 1.2, log ([CoL(OH)$_2$][H$^+$]/[CoL(OH)] = −9.82, log ([Co$_2$L(OH)$_2$][H$^+$]/[Co$_2$L(OH)] = −8.80, and log ([Cu$_2$L(OH)$_2$][H$^+$]/[Cu$_2$L(OH)]) = −8.83.
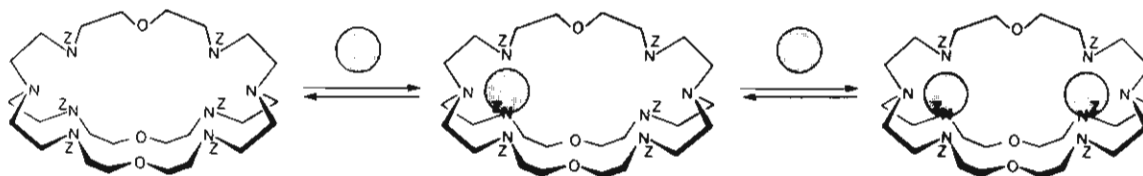

Figure 2. Schematic representation of the complexation equilibria for the mononuclear and dinuclear cryptates of the bis-tren ligand **1** (Z = H).

are needed for nitrate binding and that the binding constant increases rapidly with the number of protonated nitrogen atoms in the ligand. Similar results were obtained for chloride binding, with the constants being somewhat lower (Table II), as might be expected from the relatively weak hydrogen-bonding tendency of the chloride ion. The novel result of this potentiometric technique is the revelation of a series of nitrate complexes increasing in stability with increase in protonation of the cryptand ligand. A suggested arrangement of hydrogen bonds in the most stable (hexaprotonated) nitrate complex is indicated schematically by **2**.
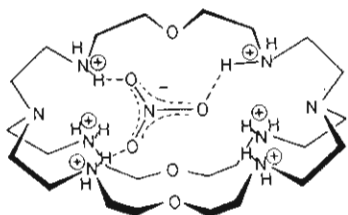
2, one of the possible hydrogen-bonding schemes for the nitrate complex of bis-tren·6HNO$_3$

The absolute values of the protonation constants of bis-tren relative to those of tren are of considerable interest because they provide insights into the influence of the cryptand structure on the basicities of the aliphatic nitrogen donor atoms and also because of their possible implications with respect to metal binding affinities. Comparison of the protonation constants in sodium perchlorate media listed in Tables I and II shows that the spread of pK's in bis-tren is over 2 times the spread of the corresponding values in the tren molecule. Adding a second proton to the monoprotonated bis-tren, HL$^+$, results in a drop in pK of 0.66, considerably more than the statistical value of slightly over 0.3, indicating a certain amount of Coulombic repulsion between the two positive nitrogen atoms. The drop in pK resulting from the third protonation step is much larger, a reflection of the fact that the first and second protons become coordinated to different tren subunits at the ends of the cryptand molecule and that the third proton

must occupy a position much closer to either one of the first two. This variation in pK's continues throughout the protonation process with large jumps between the di- and tri-protonated forms and between the tetra- and penta-protonated species and much smaller changes between the pairs involving one and two protons, three and four protons, and five and six protons. The drop in the statistical factor that occurs as protonation progresses is probably offset somewhat by increasing Coulombic repulsions, resulting in fairly even differences in the pK's of each pair ranging from 0.67 to 0.54 pK unit.[7]

The absolute values of the proton association constants of bis-tren are significantly lower than those of tren itself (0.23 log K unit for the first proton), and the differences between the two ligands rapidly increase as protonation proceeds. Although much of the lowered basicities of the bis-tren donor atoms is due to increased mutual Coulombic repulsions in the macrobicyclic molecule, this cannot be a major factor in the lowered pK's of the first protonated species. Inspection of the bis-tren molecule, **1**, illustrated schematically by Figure 2, indicates that the latter effect is probably due to the bridging ether oxygens two carbon atoms away from each of the six basic nitrogen atoms of the cryptand. The fact that an electronegative oxygen two carbons away from a basic nitrogen atom significantly lowers the basicity of the nitrogen is well-known, as can be seen from the lowered pK's of the basic amino nitrogens in such ligands as triethanolamine,[8] ((hydroxyethyl)imino)diacetic acid,[9] and ((methoxyethyl)imino)diacetic acid.[9]

Metal Ion Binding by Bis-tren. Formation of Mononuclear and Dinuclear Cryptates. The formation of constants of metal chelates of bis-tren and tren, obtained as described above, are

(7) The successive protonation steps of bis-tren may be followed by carbon-13 NMR; these studies confirm the picture outlined: Lehn, J. M.; Sonveaux, E., unpublished results.
(8) Martell, A. E.; Smith, R. M. "Critical Stability Constants"; Plenum Press: New York, 1975; Vol. 2; 1st suppl., 1982.
(9) Smith, R. M.; Martell, A. E. "Critical Stability Constants"; Plenum Press: New York, 1974; Vol. 1, 1st suppl., 1982.
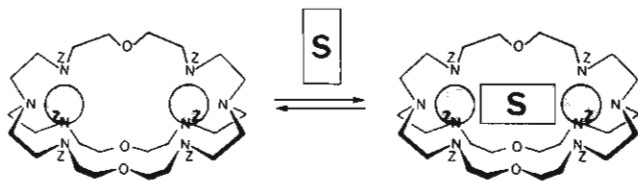
Figure 3. Schematic representation of the formation of a cascade type bridged cryptate 1-MSM by fixation of a substrate species S on the two metal ions of a dinuclear complex (Z = H).

presented in Table III. The results for bis-tren involve the formation of both mononuclear and dinuclear metal complexes as well as the formation of a series of protonated complexes of the mononuclear cryptates and also several hydroxometal complexes for both the mononuclear and the dinuclear systems. The mono- and dinuclear cryptates may be represented schematically by the dissymmetric and symmetric structures **1**-M and **1**-M_2, respectively, formulated as $[M^{2+} \subset 1]$ and $[2M^{2+} \subset 1]$; the formation equilibria are represented in Figure 2.

The stability constants of the mononuclear complexes of bis-tren and tren listed in Table III show higher stabilities for the tren complexes ranging from 1.5 to nearly 3 log units. Although the basicities of the donor nitrogen atoms in bis-tren are considerably lower than those of tren, there are additional factors involved in the formation of the bis-tren cryptates that might be expected to counteract the effect of lower basicity. All tren complexes indicated in Table III are tetradentate. On the other hand, in the case of bis-tren there are eight coordinating nitrogen donor groups, so that up to six nitrogens might be considered possibly available for coordination of the metal ions. There is also a possibility that the three ether oxygens might be involved as weak donor groups. In addition to these factors macrocyclic and cryptate effects would also be expected to provide higher stability for the cryptate complexes as the result of lowered hydration energies of the basic nitrogens in bis-tren compared to those in tren.[10,11] The fact that the stabilities of the 1:1 metal cryptates of bis-tren are considerably lower than those of tren shows that the reduced basicities of the donor nitrogen atoms in bis-tren more than counterbalance any stabilizing effects resulting from the possibility of additional coordination and from the cryptate effect. The latter is known to be very sensitive to the closeness of fit between the cryptand ligands and the metal ions coordinated within the macrobicyclic system.[12] Furthermore, these lower stabilities of the 1:1 cryptates may also indicate that the metal ions are coordinated primarily by a single tetraamine unit, leaving the four nitrogen sites at the opposite end of the cryptate relatively free; three of these basic nitrogens readily participate in the formation of the series of three protonated metal chelate species MHL^{3+}, MH_2L^{4+}, and MH_3L^{5+}.

The sequence of stability constants for the dinuclear cryptates of bis-tren is the same as for the 1:1 complexes: Co(II) < Zn(II), Ni(II) < Cu(II). The equilibrium constant for the binding of the second cation (second step in Figure 2) is lower than that of the first by factors of about 10^4-10^5. As expected, the inclusion of a second metal ion within the cryptate occurs with much lower binding affinity.

Formation of Cascade Type Bridged Species. Subsequent fixation of a substrate species S to both initially bound metal ions yields cascade type bridged species 1-M_2S (Figure 3).[2]

The dinuclear cryptates yield unique hydroxo complexes that are not formed by analogous non-cryptate complexes of these

metal ions. The affinities of the metal ions in the dinuclear bis-tren cryptate complexes for hydroxide ions are much higher than those of the metal ions in the mononuclear cryptates, as shown by differences in equilibrium constants from 2 to 6 orders of magnitude. The extremely low pK's indicate that the hydroxo ligand apparently sees both metal ions and occupies a strongly bound bridging position, forming a monohydroxo, cascade type, dinuclear species $[M(OH)M \subset 1]^{3+}$. It had been observed earlier[2b] that addition of water to an acetonitrile solution of $[2Cu^{2+} \subset 1]\cdot 4ClO_4^-$ leads to a strong decrease in the intensity of the EPR signal. In line with other related results,[13] this may be attributed to strong antiferromagnetic coupling with the two Cu(II) cations, via the hydroxo bridge in the $[Cu(OH)Cu \subset 1]^{3+}$ species and is relevant to the proposed occurrence of phenoxide bridging in dinuclear copper sites of cuproproteins.[14]

The somewhat higher pK's (around 8.8) for the addition of a second hydroxide bridge in the copper and cobalt cryptates of **1** indicate a somewhat lower affinity for the second hydroxide ion, as expected on both electrostatic and steric grounds. However, as will be shown below, the cryptate structure protects such $LM_2(OH)_2$ forms, which would not be stable with a simple acyclic polydentate ligand.

The affinities of the mononuclear bis-tren cryptates for hydroxide ion seem to be somewhat higher than with the chelates of tren, indicating possible repulsion of the negative hydroxo ligand by the uncoordinated polar nitrogen atoms of the cryptate or conversely the tendency for the remaining solvated water molecules in the mononuclear cryptate to hydrogen bond to the otherwise uncoordinated basic nitrogen atoms.

The binding of dioxygen to the dinuclear cobalt cryptate is apparently relatively weak (Table III). The green dicobalt(II) cryptate, obtained from **1** and $Co(ClO_4)_2$ under argon, reacts with oxygen to give the brown, dibridged, dioxygen cryptate containing peroxo and hydroxo bridges $[Co(O_2)(OH)Co \subset 1](ClO_4)_3$, which has been isolated;[2b] it is represented schematically by structure **3**. In solution **3** is
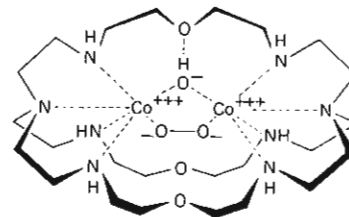
3, suggested arrangement of coordinate bonds in dibridged dioxygen complex formed from dinuclear Co(II) bis-tren cryptate

readily converted to the dihydroxo-dibridged complex so that it is never more than a minor species.

The unusually low affinity of the monohydroxo-bridged dinuclear cryptate of cobalt for molecular oxygen to give **3** may be due to steric effects related to the crowding caused by the hydroxo and peroxo bridging ligands and to the reorganization of the cryptate structure in going from a dinuclear

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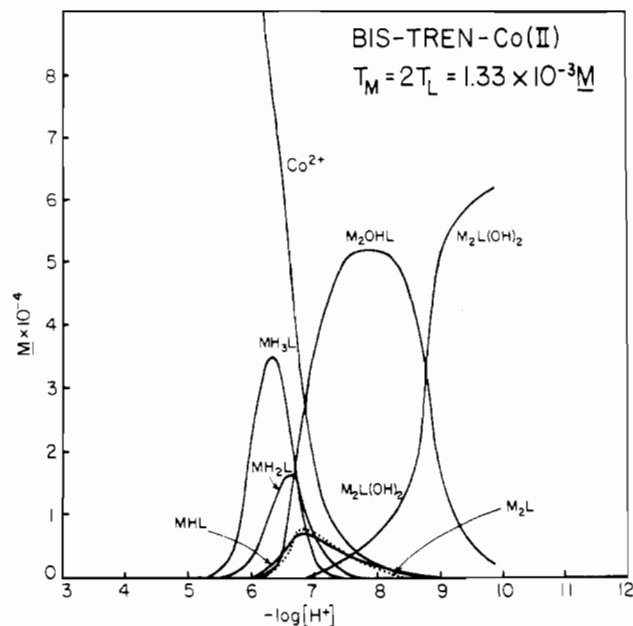
Figure 4. Distribution of complex species as a function of hydrogen ion concentration in a solution containing a 2:1 molar ratio of Co(II) to bis-tren.

hydroxo-bridged cryptate of Co(II) to a dinuclear essentially Co(II) species containing both hydroxo and peroxo bridges within the cryptate structure.

Distribution of Complex Species in Solution. The very complex nature of the aqueous solutions containing dinuclear and mononuclear bis-tren cryptates is best visualized with the aid of species distributions diagrams of the type indicated by Figures 4 and 5, for the dinuclear Co(II) bis-tren cryptates and the 1:1 Zn(II):bis-tren systems, respectively. When the molar ratio of Co(II) to bis-tren is 2:1, the distribution diagrams in Figure 4 indicate that the 1:1 mononuclear bis-tren cryptate is first formed at low pH. The first species to appear are the protonated mononuclear metal cryptates, each giving way to the next as the pH is increased. Before any of these protonated mononuclear species disappear however, the dinuclear cryptate, the monohydroxo-bridged dinuclear cryptate, and the dihydroxo-bridged dinuclear cryptate begin to appear in succession. It is interesting to note that the "so-called" unhydrolyzed dinuclear cryptate, Co_2L^{2+}, is only a relatively minor species in solution. In neutral solution the major complex form is the hydroxo-bridged dinuclear cryptate, which gives way to the dihydroxo-bridged species at higher pH. The preponderance of the hydroxo forms in the dinuclear cryptate provides an interesting illustration of the ability of dinuclear cryptate complexes to form cascade type secondary complexes with various anions (in this case the hydroxide anion). Such complexes do not exist in solutions of analogous non-cryptate
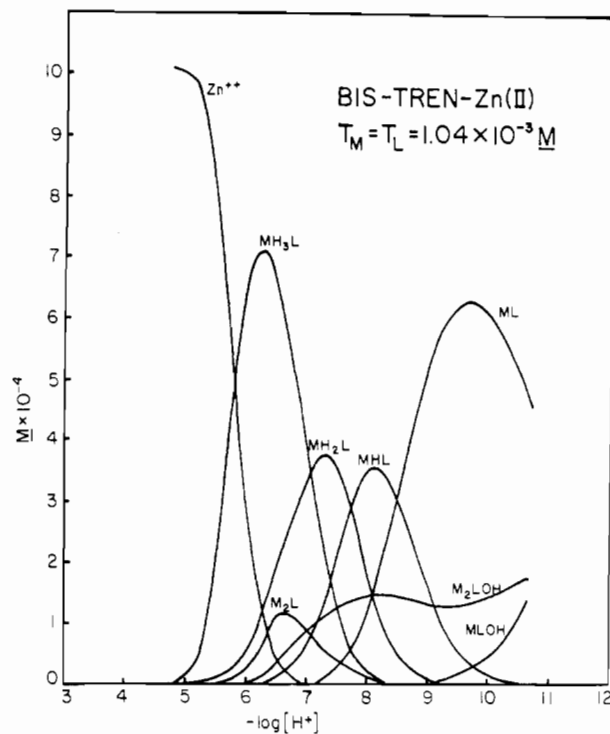
Figure 5. Distribution of complex species as a function of hydrogen ion concentration in a solution containing a 1:1 molar ratio of Zn(II) to bis-tren.

complexes such as those of tren.

The distribution curves of the 1:1 bis-tren:Zn(II) system indicate the preponderance of the protonated mononuclear metal cryptates in weakly acid, neutral, and weakly alkaline solutions. The "normal" zinc cryptate does not predominate until the pH is increased above ~8.5. It is interesting to note, however, that the tendency to form dinuclear cryptates even in this system is considerable and that some of the mononuclear species disproportionates to give an appreciable concentration of the dinuclear chelate around pH 6–7. The latter rapidly gives way to the more stable monohydroxo-bridged dinuclear chelate, which is a minor but significant species above pH 7. The high affinity of the dinuclear chelate in this system for the bridging hydroxide ion is illustrated by the fact that it predominates over the hydroxo form of the mononuclear cryptate and is first formed in solution at 3 pH units below the pH at which the mononuclear cryptate hydrolyzes.