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Registry No. *tc*-2 (L = pap), 84027-71-4; *tc*-**2** (L = tap), 81600-80-8; *cc*-3 (L = tap), 84049-23-0; *tc*-**5** (L = pap), 84027-70-3; *tc*-**5** (L = tap), 84027-73-6; *tc*-**5** (L = pap), 84027-78-1; *cc*-**6** (L = tap), 84049-25-2; *tc*-**7** (L = pap), 84027-80-5; *tc*-**8** (L = pap), 84027-77-0; $AgClO_4$, 7783-93-9; MeCN, 75-05-8; PhCN, 100-47-0; *tc*-$[Ru(PhCN)_2(tap)_2](ClO_4)_2$, 84027-75-8; *tc*-$[Ru(OH)_2(pic)(pap)_2](ClO_4)_2$, 84027-82-7; py, 110-86-1.

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Stabilities of Mononuclear and Dinuclear Macrocyclic Complexes of 1,4,7,13,16,19-Hexaaza-10,22-dioxacyclotetracosane (bisdien)

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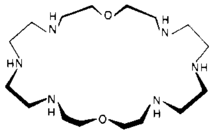
Potentiometric equilibrium studies of the stability constants of the macrocyclic metal complexes of 1,4,7,13,16,19-hexaaza-10,22-dioxacyclotetracosane (bisdien) with Cu(II), Co(II), Ni(II), and Zn(II) are reported. Equilibrium data are determined for the formation of mononuclear and dinuclear chelates of these metal ions, as well as several protonated and hydroxo chelates. The ligand is flexible enough to form stable mononuclear macrocyclic complexes in which from four to six of the basic nitrogen donors seem to be coordinated to the metal ion. The dinuclear complexes are less stable than those of the closely related cryptand ligand bistren, but the dinuclear Cu(II) chelate is sufficiently stable to form extensively in solution and is further stabilized by a bridging hydroxide ion in neutral- and high-pH solution. The dinuclear complexes of Co(II) and Cu(II) are stabilized by secondary ligands that provide two- or three-atom bridges between the metal ions. Thus neutral imidazole and the imidazolate anion form stable, cascade type, bridged dinuclear Cu(II) complexes of the macrocycle. Dioxygen forms a stable dibridged (peroxo- and hydroxo-bridged) dicobalt complex. Ethylenediamine and glycine do not appear to be bridging donors for dinuclear bisdien complexes, but ethylenediamine combines with the dicopper(II) complex of the macrocyclic ligand to form relatively weak mixed-ligand complexes.

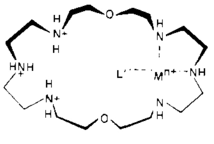
Introduction

Macrocyclic ligands containing two chelating subunits linked by two bridges may form both mononuclear and dinuclear complexes with metal cations. In the latter, the distance and arrangement in space of the two metal centers are determined by the structure of the bridges, whereas their properties depend on the nature of the chelating sites; furthermore, with suitable macrocycles, cascade complexes may form by subsequent uptake of a substrate bridging the two metal ions (for general considerations, see ref 1).

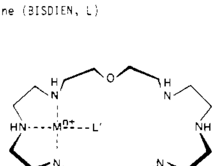
The macrocyclic hexamine bisdien (1,4,7,13,16,19-hexaaza-10,22-dioxacyclotetracosane or [24]ane-N_6O_2 (**1**)) is such a bis chelating macrocycle: it contains two diethylenetriamine units separated by two five-atom bridges. Although the ether oxygens located at the centers of these bridges may have weak coordinating tendencies toward certain metal ions, they may be neglected in considering the complexes that are formed with first-row transition metals described in this report. It is of interest to determine whether this macrocyclic hexamine, **1**, will form stable mononuclear complexes of the type indicated by **2** and **3**. The flexibility of the two five-atom bridges probably would allow the six basic nitrogen atoms in the ligand to coordinate to a single metal ion, although with considerable loss of entropy. Conceivably, dinuclear complexes such as **4** may also form, especially in the presence of additional mono-, di-, or tridentate ligands, resulting in the formation of mixed-ligand dinuclear complexes such as **5** and **6**.



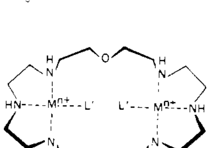
1 1,4,7,13,16,19-hexaaza-10,22-dioxacyclotetracosane (BISDIEN, L)



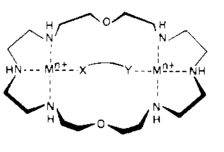
2 Protonated mononuclear BISDIEN chelate, $MH_3L'L^{(3+n)+}$ (L' = solvent molecule)



3 Mononuclear BISDIEN chelate $ML'L^{n+}$ (L' - solvent molecule)



4 Binuclear BISDIEN chelate, $M_2L'_2L^{2n+}$ (L' = solvent molecule)



5 Binuclear dibridged BISDIEN chelate, $M_2(X\text{-}Y)L^{2n+}$ (X-Y = neutral bidentate ligand)

The synthesis of **1** has been performed in the course of the study of the macrobicyclic dinucleating ligand bistren[2] (7,19,30-trioxa-1,4,10,13,16,22,27,33-octaazabicyclo[11.11.11]pentatriacontane), and a more direct procedure has been developed more recently.[3] In the presence of azide ions, **1** forms a dinuclear copper(II) cryptate, $[(N_3)_2Cu,Cu(N_3)_2 \subset \mathbf{1}]$, in which the two metal ions are contained inside the macrocyclic ligand; its structure and magnetic properties have been studied.[3] Recent papers have reported the formation of cascade complexes in which the two metal ions of the dinuclear copper(II) complex of **1** are bridged by an imidazolate[4] or hydroxide[5] anion.

In view of these results, it appeared of interest to determine the possible role of bridging ligands in stabilizing and pro-

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(6) Schwarzenbach, G.; Flaschka, H. "Complexometric Titrations", 2nd English ed.; Methuen & Co.: London, 1969.

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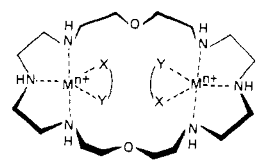
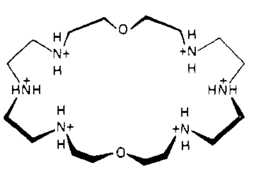
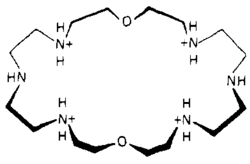


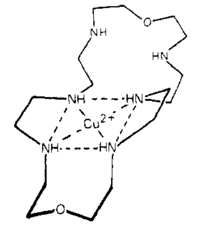
6 Dinuclear mixed-ligand BISDIEN chelate, $M_2(X-Y)_2L^{2n+}$
(X-Y = neutral bidentate ligand)



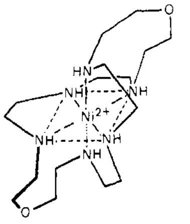
7 Hexaprotonated BISDIEN, H_6L^{6+}



8 Tetraprotonated BISDIEN (H_4L^{+})



9 Mononuclear Cu(II)-BISDIEN Chelate, CuL^{2+}



10 Mononuclear Ni(II)-BISDIEN Chelate, NiL^{2+}

moting the formation of dinuclear complexes of **1** in aqueous solution.

In the present paper equilibrium studies of the formation of mononuclear and dinuclear complexes of **1** are reported for systems with and without auxiliary ligands, some of which may serve as bidentate coordinating linkages between two transition-metal ions. Computer-assisted analysis of the equilibrium data is employed to sort out the various species formed in these complex systems, as well as to determine the equilibrium constants involved.

Experimental Section

The ligand bisdien was prepared as a colorless crystalline hexahydrochloride after detosylation of the macrocyclic amino tetratosylate[2] or hexatosylate.[3] Stock solutions (0.0200 M) of reagent grade metal nitrates were prepared in double-distilled water, and their concentrations were determined by potentiometric titrations with EDTA (ethylenediaminetetraacetic acid). The acid forms of the ligand were titrated with carbonate-free solutions of 0.100 M KOH, prepared from Dilut-it ampules, standardized with potassium acid phthalate. Potassium nitrate, the supporting electrolyte, was obtained as reagent grade quality. The secondary ligands ethylenediamine dihydrochloride and imidazole free base were also obtained as reagent grade materials. Imidazole was recrystallized from benzene, and ethylenediamine was purified by crystallization from 50% ethanol/50% H_2O as the dihydrochloride.

Potentiometric Equilibrium Measurements. Potentiometric studies of bisdien in the absence and in the presence of metal ions were carried out with a Corning Model 21 pH meter fitted with blue-glass and calomel reference electrodes 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 KNO_3. The concentrations of the experimental solutions were either 0.0010 or 0.0020 M in ligand. Equilibrium measurements were made on solutions containing 1:1 and 2:1 molar ratios of metal ion to bisdien. Ternary systems containing metal, bisdien, and auxiliary ligand were studied at molar ratios of 2:1:1 and 2:1:2. For the systems described, equilibrium data were measured only for homogeneous solutions; precipitation was observed only at high pH values in systems having a 2:1 molar ratio of Co(II) or Ni(II) to bisdien.

Computations. The proton association constants of bisdien were determined by using the program PKAS.[7] The equilibrium constants with metal ions at the appropriate ratios described above were obtained through the algebraic solution of mass balance and charge balance equations evaluated at each equilibrium point of the formation curves. Detailed refinements of the preliminary constants were carried out with the program BEST written in this laboratory.[8] The input for the program BEST consists of entering the components, the concentrations of each component, the initial estimates of the equilibrium constant for each species thought to be present in terms of these solution components, and the experimentally determined equilibrium data. The program sets up simultaneous mass balance equations for all the components present at each increment of base added and solves for the concentration of each species present. Equilibrium constants are varied in order to obtain minimization of the difference between the calculated and observed values of $-\log [H^+]$. The error estimates reported are measures of the pH fit over the entire potentiometric equilibrium curve. No attempt was made to "invent" additional species for the purpose of obtaining a better fit of the experimental data. The species introduced were limited to those that could be justified on the basis of established principles of coordination chemistry in solution.

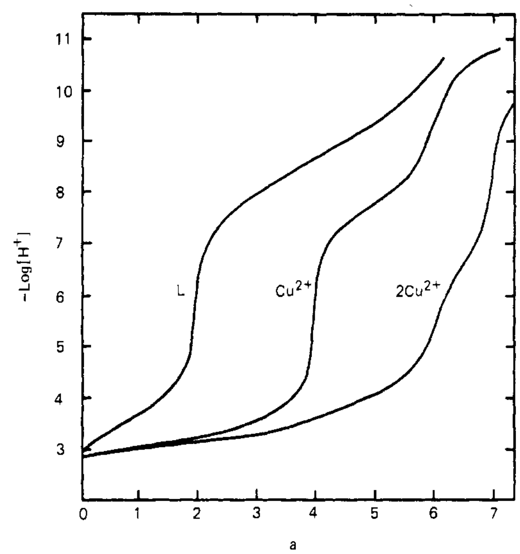


Figure 1. Potentiometric equilibrium curves for bisdien$(HCl)_6$–copper(II) systems at 25.00 ± 0.05 °C and μ = 0.1000 M (KNO_3): $T_L = 2.310 \times 10^{-3}$ M (L alone); $T_M = 1.547 \times 10^{-3}$ M, $T_L = 1.664 \times 10^{-3}$ M (1:1 Cu-L); $T_M = 2.484 \times 10^{-3}$ M, $T_L = 1.336 \times 10^{-3}$ M (2:1 Cu-L). a = moles of standard KOH added per mole of ligand present; there are approximately 10 equilibrium points per "a" value.

Table I. Protonation Constants of bisdien (μ = 0.100 M (KNO_3); t = 25.00 °C)

bisdien[a]		dien[b]	
$\log K^H_1$	9.65	$\log K^H_1$	9.84
$\log K^H_2$	8.92		
$\log K^H_3$	8.30	$\log K^H_2$	9.02
$\log K^H_4$	7.64		
$\log K^H_5$	3.81	$\log K^H_3$	4.23
$\log K^H_6$	3.26		

[a] σ = 0.0025. [b] Reference 12.

Results

Metal-Free bisdien. In the absence of added complexing metal ions the potentiometric equilibrium curve of bisdien$(HCl)_6$ (**7**), illustrated in Figure 1, is seen to possess a sharp inflection at a = 2 (where a = moles of base added per mole of ligand) followed by an extensive buffer region from a = 2 to a = 6. The first inflection corresponds to completion of the neutralization of the two most acidic substituted ammonium ions, the more acidic of which is extensively dissociated in aqueous solution at the starting point (a = 0). The buffer

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(7) Motekaitis, R. J.; Martell, A. E. *Can. J. Chem.* **1982**, *60*, 168.
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Table II. log (Stability Constants) of Cu(II), Ni(II), Co(II), and Zn(II) Complexes of bisdien (μ = 0.100 M KNO_3; t = 25.00 °C)

	log Q							
	Cu(II)		Ni(II)		Co(II)		Zn(II)	
quotient, Q	bisdien	dien[a]	bisdien	dien[a]	bisdien	dien[a]	bisdien	dien[a]
[ML]/[M][L]	16.46 (2)[b]	15.9	13.65 (1)	10.5	9.73 (1)	8.0	10.66 (1)	8.8
$[M_2L]/[M][ML]$	10.84 (2)		*c*		2.7 (7)		4.20 (1)	
$[MHL]/[ML][H^+]$	8.01 (2)		7.17 (1)		7.58 (1)		7.58 (1)	
$[MH_2L]/[MHL][H]$	7.46 (2)		5.03 (1)		5.97 (1)		5.63 (1)	
$[MH_3L]/[MH_2L][H]$	3.45 (2)		*c*		*c*		*c*	
$[MOHL][H^+]/[ML]$	−10.63 (3)		*c*		<−11.8		−10.13 (1)	
$[M_2OHL][H]/[M_2L]$	−6.51 (1)		*c*		*c*		>−7[d]	
$[M_2(OH)_2L][H]/[M_2(OH)L]$	−10.40 (1)		*c*		*c*		*c*	

[a] Values for dien[12] are included for comparison. [b] Figures in parentheses represent σ in the last digits. [c] Species not found. [d] Since zinc hydroxide precipitates, it is only possible to estimate this constant.

region occurring at high pH corresponds to the dissociation of the remaining four substituted ammonium groups of the ligand in sequential overlapping steps. All six deprotonation reactions were found to occur in a pH range suitable for the calculation of protonation constants from the potentiometric data. The log values of the protonation constants obtained at 25.00 °C, μ = 0.100 M, as defined by eq 1 and 2, are 9.75, 8.92, 8.30, 7.64, 3.81, and 3.26. These association constants are listed in Table I, with the corresponding values of diethylenetriamine (dien) for comparison.

$$H_{n-1}L^{(n-1)+} + H^+ \rightleftharpoons H_nL^{n+} \quad (1)$$

$$K^H{}_n = [H_nL^{n+}]/[H_{n-1}L^{(n-1)+}][H^+] \quad (2)$$

Metal Chelates of bisdien. The potentiometric equilibrium curves of 1:1 and 2:1 ratios of metal ion to ligand (Figures 1 and 2) illustrate the type of behavior observed for Zn(II) ion and for the transition-metal ions Co(II), Ni(II), and Cu(II). The curves for Ni(II) and Co(II) in Figure 2, which were similar to those of Zn(II), indicate that these metal ions do not combine with the ligand until the first two protons of the ligand have been neutralized, whereas Cu(II) reacts more strongly at considerably lower pH and displaces protons from the hexaprotonated form of the ligand. The 1:1 curve for Cu(II) shows that the initial complex formed contains two protonated basic nitrogen atoms, which are neutralized at higher pH. For the 2:1 system (Figure 1) all six protons of **7** are displaced by Cu(II) above pH 5 but the equilibrium curve indicates an additional hydrolysis step involving the neutralization of an additional proton from the complex at intermediate pH.

The 1:1 curves for Co(II), Ni(II), and Zn(II), illustrated by Figure 2 for Ni(II) and Co(II), indicate that the tetraprotonated form of the ligand combines with these metal ions with the displacement of protons from three basic nitrogen atoms of the ligand. The remaining proton is displaced at higher pH with the formation of a chelate compound in which the completely deprotonated ligand is coordinated to the metal ion. For these transition-metal ions 2:1 ratios of metal ion to ligand were found to result in precipitation of metal hydroxide from neutral to weakly alkaline solution and were not further investigated.

The equilibrium constants that were found necessary to account for the potentiometric equilibrium data of the type illustrated in Figures 1 and 2 are listed in Table II, together with the corresponding values for dien (diethylenetriamine). It is seen that computer analysis of the data reveals the existence of a considerably larger number of species than those that were obvious by visual examination of the potentiometric equilibrium curves. In addition to the two apparent protonated species of the 1:1 copper complex system, a third less stable protonated form was found to be necessary to explain the low-pH data. Also the high-pH hydroxo form of the mononuclear Cu(II) complex is not obvious from the equilibrium curves but was required for a computer fit of the data. Not surprisingly, the dinuclear Cu(II) complex forms two hydroxo species. One of these, the monohydroxo chelate, is obvious from the equilibrium curve, but the dihydroxo form is not. Of the two protonated forms found for Co(II) and Zn(II), only one was apparent from visual inspection of the equilibrium curves. Although weak dinuclear complexes were detected for Zn(II) and Co(II), no evidence for an analogous dinuclear Ni(II) chelate was provided by the equilibrium data. The formation of a dinuclear monohydroxo Zn(II) chelate with a pK of ~7 was found to improve the computer fit of the data, but similar evidence was not found for Co(II).

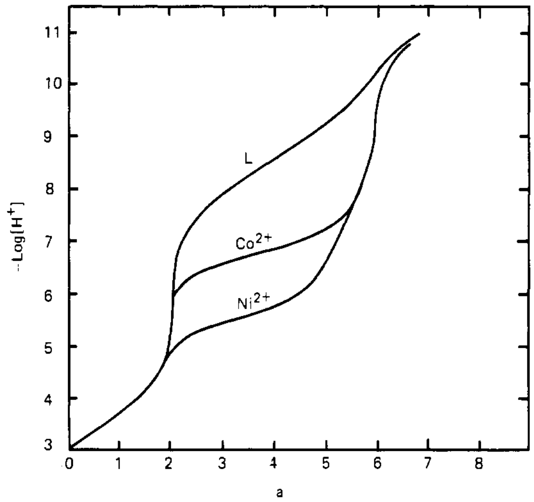

Figure 2. Potentiometric equilibrium data for 1:1 cobalt(II) and nickel(II) systems with bisdien at 25.00 ± 0.05 °C and μ = 0.1000 M (KNO_3): $T_L = 2.310 \times 10^{-3}$ (Co^{2+}); $T_M = 2.365 \times 10^{-3}$ M (Ni^{2+}); $T_L = T_M = 2.322 \times 10^{-3}$ M. a = moles of KOH added per mole of bisdien present.

Mixed-Ligand Complexes. Mixed-ligand complexes of Co(II)–bisdien with glycine or ethylenediamine (en) as secondary ligands were investigated, in view of the successful use of these secondary ligands in stabilizing oxygen adducts of the binuclear complexes of the analogous hexaamine 1,4-bis(bis(2-aminoethyl)aminomethyl)benzene (pxbde).[9] The systems investigated contained 2:1:1 and 2:1:2 molar ratios of Co^{2+}–L–L′, where L′ is the secondary ligand, ethylenediamine or glycine. Analysis of the potentiometric equilibrium data obtained gave no evidence for the formation of mixed-ligand complexes with glycine, since the equilibrium data were fully explained by the assumption that separate 1:1 Co(II)–bisdien and 1:1 and 1:2 Co(II)–glycinate complexes were formed. Ethylenediamine, on the other hand, gave evidence for the formation of stable mixed-ligand complexes containing

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Table III. Stability Constants of Mixed-Ligand Complexes of Co(II) with en and bisdien and of Cu(II) with Im and bisdien[a] ($\mu = 0.100$ M (KNO_3); $t = 25.00$ °C)

$[(bd)(en)Co_2]/([bd][en][Co^{2+}]^2) = 10^{18.28}$

$[(bd)(en)_2Co_2]/([bd][en]^2[Co^{2+}]^2) = 10^{21.94}$

$[(bd)ImCu_2]/([bd][Im][Cu]^2) = 10^{30.1\,(1)}$

$[(bd)(en)Co_2]/([(bd)Co_2][en]) = 10^{5.7}$

$[(bd)(en)_2Co_2]/([(bd)(en)Co_2][en] = 10^{3.7}$

$[(bd)ImCu_2]/([(bd)Cu_2][Im]) = 10^{3.8\,(1)}$

$[(bd)ImCu_2]/([(bd)ImCu_2][H^+]) = 10^{3.86\,(5)}$

[a] Abbreviations bd = bisdien; Im = imidazole; en = ethylenediamine.

Table IV. Equilibrium Constants for the Formation of Dioxygen Complexes of Co(II)–bisdien ($\mu = 0.100$ M (KNO_3); $t = 25.00$ °C)

$[(bd)Co_2O_2(OH)][H^+]/([(bd)Co_2]P_{O_2}) = 10^{-3.29}$

$[(bd)Co_2O_2(OH)_2][H^+]/[(bd)Co_2O_2(OH)] = 10^{-8.25}$

$[(bd)Co_2O_2(OH)_3][H^+]/[(bd)Co_2O_2(OH)_2] = 10^{-9.36}$

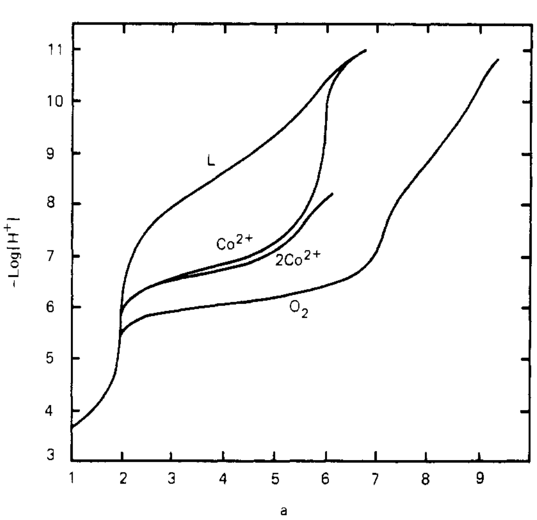

Figure 3. Potentiometric equilibrium data for the Co(II)–bisdien system under anaerobic conditions and in the presence of dioxygen measured at 25.00 ± 0.05 °C and $\mu = 0.1000$ M (KNO_3): $T_L = 2.310 \times 10^{-3}$ M (ligand alone); $T_L = T_M = 2.37 \times 10^{-3}$ M (1:1 Co–L anaerobic); $T_L = {}^1/_2 T_M = 1.93 \times 10^{-3}$ M (2:1 Co–L anaerobic); $P_{O_2} = 1.00$ atm, $T_L = {}^1/_2 T_M = 1.92 \times 10^{-3}$ M (2:1Co–L anaerobic). *a* = moles of base added per mole of bisdien present; there are 10 or 11 equilibrium points per "*a*" value.

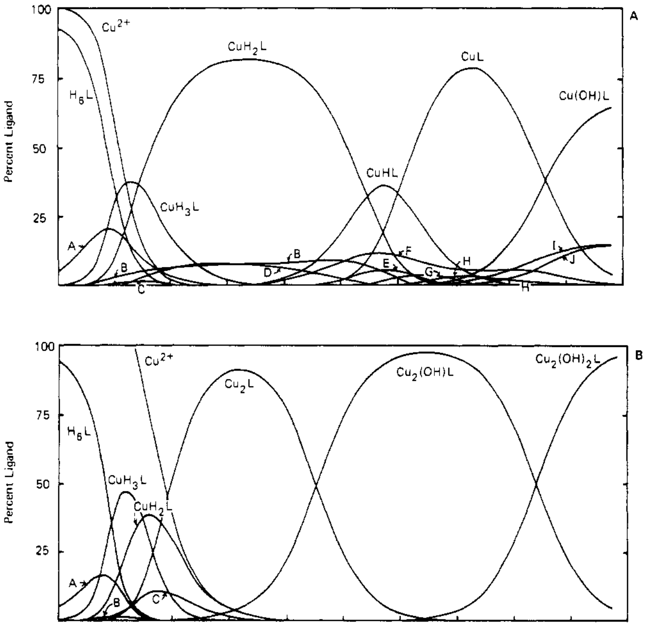

Figure 4. Species distribution diagram of the copper(II)–bisdien systems as a function of $-\log [H^+]$: (A) $T_L = T_M = 1.000 \times 10^{-3}$ M, A = H_5L, B = H_4L, C = Cu_2HL, D = Cu_2L, E = H_3L, F = $Cu_2(OH)L$, G = H_2L, H = HL, I = L, J = $Cu_2(OH)_2L$; (B) $T_L = 1.000 \times 10^{-3}$ M, $T_M = 2.000 \times 10^{-3}$ M, A = H_5L, B = H_4L, C = Cu_2HL. For the 2:1 system the percentage species is represented relative to the total bisdien present.

both 1 and 2 mol of the secondary ligand/mol of metal ion, and the formation constants thus obtained are given in Table III. These stability constants show that the first mole of ethylenediamine combines with the dinuclear complex with considerable affinity (log *K* = 5.9), while the second mole adds with considerably less affinity, as expected (log *K* = 3.6).

In view of the report by Caughlin et al.[4] of the isolation of a binuclear Cu(II)–bisdien chelate containing a negative imidazolate bridging ligand from methanol solution, imidazole was also investigated as a secondary ligand for the aqueous dinuclear Cu(II)–bisdien system. For aqueous solutions containing 2:1:1 molar ratios of Cu(II)–L–L′, the potentiometric equilibrium data obtained show the formation of a mixed-ligand complex with neutral imidazole at low pH. This initial complex was found to have a pK of 3.86 (see Table III), thus indicating the possibility of formation of an imidazolate bridge between the metal ions.

Cobalt Dioxygen Complex Formation. Potentiometric equilibrium data for the dinuclear Co(II)–bisdien system in the presence of dioxygen at 1-atm pressure gave evidence for the formation of a stable dibridged dioxygen complex similar to those reported for tren (tris(2-aminoethyl)amine) and bistren and for other polyamine–Co(II) complexes containing less than five donor groups per metal ion. Potentiometric equilibrium curves for the Co(II)–bisdien–dioxygen system are illustrated in Figure 3, and the corresponding equilibrium constants are listed in Table IV. The buffer region for the 2:1 system under 1 atm of oxygen illustrates the formation of a very stable dioxygen complex requiring 7 mol of base/mol of ligand or metal ion, thus providing evidence for the stoichiometry of formation of the dibridged complex. This system differs, however, from the analogous dioxygen complexes cited above in the existence of two additional hydrolysis steps at higher pH, presumably involving the coordination of two additional hydroxide ions with the metal ions of the dioxygen complex, as indicated by the p*K*s listed in Table IV.

Species Distribution Curves. On the basis of the equilibrium data in Tables I and II the distributions of individual Cu(II) complex species were calculated as a function of pH for 1:1 and 2:1 molar ratios of Cu(II)–ligand, and the results are illustrated in Figure 4. The most striking feature of the 1:1 system (Figure 4A) is that the most predominant complex species is the diprotonated Cu(II)–bisdien chelate, which is present at higher concentration than any other component between pH 3.5 and 7.5. The normal (deprotonated) Cu(II)–bisdien complex predominates between pH 8 and 10.5, while at high pH the monohydroxo species becomes the main complex present in solution. A very remarkable aspect of this 1:1 system is that none of the mononuclear complexes, CuH_2L, CuHL, CuL, or CuOHL, ever approach 100% formation and that free ligand is present in appreciable amounts throughout the pH range from 2 to 12. This behavior is due to the fact that a considerable amount of the dinuclear complex Cu_2L^{4+} is present in solution from pH 3 to 7 and is superceded by successive formation of the binuclear monohydroxo chelate $Cu_2(OH)L^{3+}$ and finally the dinuclear dihydroxo chelate $Cu_2(OH)_2L^{2+}$ as the pH is further increased. Thus we have the situation such that all Cu(II) is complexed while some of

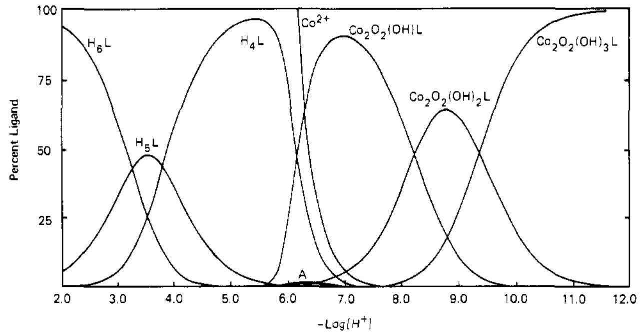

Figure 5. Species distribution diagram of the 2:1 Co–bisdien system under oxygen as a function of $-\log [H^+]$: $T_L = {}^1/_2T_{Co^{2+}} = 1.000 \times 10^{-3}$ M; $P_{O_2} = 1.00$ atm. A designates low concentration levels for H_3L, CoHL, and CoH_2L.

the ligand remains uncoordinated, because of its strong tendency to form dinuclear copper(II) complexes in solution.

The system containing a 2:1 molar ratio of Cu(II)–bisdien is much simpler than the corresponding 1:1 solution, as illustrated in Figure 4B. In this case it is seen that the mononuclear protonated species are formed only at low pH and never become more than minor constituents of the solution. Formation of the dinuclear bisdien complex starts between pH 3 and 4 and from pH 4 to 6.5 becomes the predominant complex. As the pH is further increased, it is replaced by the dinuclear monohydroxo complex and finally by the dinuclear dihydroxo complex. Above pH 5.5 all of the ligand is converted to dinuclear complexes and the metal ion is completely complexed.

The formation of stable dinuclear complexes of the type illustrated for Cu(II) was found not to occur for Co(II), Ni(II), and Zn(II). The higher coordination numbers of these metal ions, combined with the fact that each end of the macrocycle provides only three basic nitrogen groups per metal ion, resulted in the formation of weaker dinuclear complexes which do not prevent precipitation of the metal ion as the pH is increased.

Attempts to stabilize the dinuclear complexes with secondary ligands gave mixed results. In the presence of glycine no mixed-ligand complexes could be detected, so that the system containing 2:1:2 molar ratio of Co(II)–bisdien–glycine turned out to be simply a mixture of the 1:1 Co(II)–bisdien complex and the 1:2 Co(II)–glycinate complex. With ethylenediamine as a secondary ligand some mixed-ligand complexes of Co(II) and bisdien were obtained. A species distribution curve for this system (not shown) revealed, however, that the mixed-ligand complexes never account for more than a third of the Co(II) or bisdien present in solution, and the single-ligand complexes of bisdien and ethylenediamine were found to predominate over the entire pH range (pH 6–12) in which apprecibale complex formation occurs.

In accordance with expectations,[4] imidazole serves as an effective secondary ligand in the dinuclear Cu(II) system, even when only 1 mol of imidazole is added per 2 mol of copper ion in solution. Stabilization of both Cu(II) ions in the dinuclear complex is evident on the basis of the lack of formation of hydroxo species at high pH, as observed (Table II, Figure 1) in the absence of a secondary ligand.

The distribution of ligand and metal complex species formed in a system containing a 2:1 molar ratio of Co(II)bisdien in the presence of excess oxygen is illustrated in Figure 5. It is seen that, in contrast to the low degree of formation of the dinuclear complexes in the absence of oxygen, dinuclear species begin to form at pH 6 and become predominant at pH 7 and above. It is interesting to note that the mononuclear species CoHL and CoH_2L are present between pH 6 and 7 at very low concentrations. The first dinuclear complex to form contains 1 mol of dioxygen/mol of ligand and 1 mol of hydroxide ion/mol of ligand. At higher pH two additional hydroxide ions become coordinated to this complex in successive steps. Above pH 7 the dinuclear dioxygen complexes predominate in solution and account for nearly all of the metal ion and ligand species (>99%).

Discussion

Ligand Protonation Constants. Since protons distribute themselves among the available basic nitrogen atoms of a polyamine ligand so as to minimize Coulombic repulsions, the first four protonation reactions in Table I are assigned to the 1-, 7-, 13-, and 19-nitrogens (**8**). The decrease of proton affinity observed as a function of the number of protonated nitrogens is, of course, expected, and the tetraprotonated ligand **8** should have an extended structure in solution with the positive nitrogens as far apart as possible. The much lower affinity of the ligand for the fifth and sixth protons is due to the fact that these protonation reactions occur at the central nitrogens at each end of the macrocycle (N4 and N16). Since each end of the molecule may be considered to consist of a diethylenetriamine unit, there is a close analogy between the protonation constants of bisdien and those of dien itself, which are listed in Table I for comparison. It is interesting to note that all the p*K*s of bisdien are considerably lower than the corresponding values for dien. This effect is due mainly to the electronegativity of the bridging oxygen atoms and is similar to the effects of β-hydroxyl oxygens and of β-ether oxygens observed for other amines and polyamines such as triethanolamine[12] and bistren.[10]

Metal Chelate Stability Constants. The stability constants listed in Table II may be interpreted in terms of the basicity (i.e., proton affinity) and structure of the ligand and of the coordination number and coordination tendencies of the metal ions. Although the lower basicities of the nitrogen donor atoms of bisdien would tend to make each metal–nitrogen coordinate bond weaker than the corresponding coordinate bonds of dien, all of the bisdien stabilities listed for 1:1 metal complexes in Table II are higher for bisdien than for dien. This behavior is a result of the fact that bisdien has six coordinating nitrogens while dien has only three, so that the former may form four strong coordinate bonds to Cu(II) (formula **9**) and perhaps a larger number of coordinate bonds for Ni(II), Co(II), and Zn(II) (formula **10**). Therefore it seems that the bisdien macrocycle, which is relatively flexible, may use both dien units for the coordination of a single metal ion. This behavior is quite different from that of bistren, for which all metal complexes have been found to have stability constants lower than those of the corresponding tetradentate amine tren. It appears that the bicyclic nature of bistren makes it more difficult for the two tetraamine coordinating groups of that ligand to coordinate with a single metal ion, even for metal ions with coordination numbers higher than 4 such as Ni(II) and Co(II).

For all transition-metal ions investigated, and Zn(II), bisdien forms both monoprotonated and diprotonated 1:1 metal chelates, probably involving coordination of the metal ion by one dien unit and the coordination of one or two protons by the other dien unit, with the two triamine moieties oriented as far apart as possible to minimize Coulombic repulsions, as indicated by **11** for the diprotonated mononuclear Cu(II). In this respect bisdien shows considerable resemblance to bistren, which forms a similar series of 1:1 metal chelates having several protonated forms.

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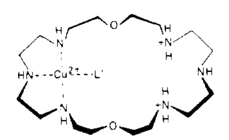
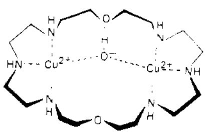
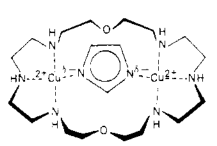


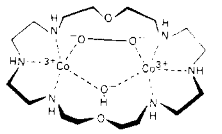
11 Diprotonated mononuclear Cu(II)-BISDIEN complex CuH_2L^{4+}



12 Hydroxo-bridged binuclear Cu(II)-BISDIEN complex, Cu_2LOH^{3+}



13 Imidazolate-bridged binuclear Cu(II)-BISDIEN complex $Cu_2L'L^{3+}$



14 Dibridged dioxygen complex $Co_2O_2(OH)L^{3+}$ formed from the binuclear cobalt(II)-BISDIEN chelate, Co_2L^{4+}

The relatively low basicities of the nitrogen donors in bisdien are evident in the formation of dinuclear chelates, the stabilities of which are listed in Table II. All dinuclear complexes, except the one containing Cu(II), are very weak with respect to the addition of the second metal ion, as indicated by the low stability constants listed for Co(II) and Zn(II) and by the fact that precipitation of the second metal ion as the hydroxide occurs in neutral and alkaline solution. The fact that no dinuclear complex was detected potentiometrically for Ni(II) is ascribed to possible strong octahedral coordination in the 1:1 metal chelate, thus making it more difficult to rearrange the complex by adding a second metal ion.

The behavior of the dinuclear Cu(II) complex in alkaline solution is interesting in that it reveals an additional resemblance of the coordinating behavior of bisdien to that of bistren. The low pK (6.51) for the formation of the monohydroxo binuclear chelate is an indication of the very strong binding of the hydroxide ion. In view of the fact that the Cu(II)–dien chelate has very little tendency to hydrolyze,[12] it appears that the hydroxide ion is probably bridged between the two metal ions (**12**). The high stability of this species is further indicated by the relatively high pK (10.4) for addition of a second hydroxide ion to the dinuclear complex. The crystal structure of a hydroxo-bridged dinuclear Cu(II) complex of bisdien has been determined recently and shown to display strong antiferromagnetic coupling.[5] Similar hydroxo bridging has been reported for several bis(copper(II)) complexes,[13] among which is that of the macrobicyclic cryptand bistren.[2,10]

Mixed-Ligand Chelates. As indicated in Table III, only two metal ions (Cu(II) and Co(II)) were investigated for mixed-ligand complex formation, for the reasons cited above. The relatively strong binding of a single imidazole to the dinuclear Cu(II)–bisdien complex and the stepwise dissociation of two protons observed in the binding of a single imidazole suggest a bridged structure, **13**, analogous to the reported structure.[4] The coordination of an additional imidazole to each Cu(II) ion observed in the latter structure is probably weak, and its place is probably taken up by two water molecules in aqueous systems in which only one bridging imidazole is available. The tendency of the dinuclear mono(imidazole) complex to bind additional imidazole donors was not investigated in the present study.

The weak tendency of the dinuclear Co(II)–bisdien complex to add 1 or 2 mol of secondary ligand may be due to steric repulsions between the secondary donor molecules and the pair of five-atom bridges between the coordination spheres of the two metal ions. The weak mixed-ligand complexes that do form probably have distorted configurations for both the macrocycle and the auxiliary ligands, with considerable deviation of the metal–ligand bonds from the preferred octahedral 90° angles around the metal ion.

Dioxygen Complexes. The relatively high stability of the dibridged (μ-peroxo)(μ-hydroxo) dinuclear Co(II)–bisdien complex, represented by **14**, provides an interesting contrast to the corresponding dioxygen complex of bistren. The bisdien dioxygen complex is formed as a major component in the solution as indicated by the species distribution curve for the dinuclear Co(II)–dioxygen–bisdien system (Figure 5). In the case of bistren, however, the analogous dioxygen complex is never more than a minor constituent in solution; this is ascribed to low stability resulting from steric effects and the strong tendency of the bistren dinuclear Co(II) complex to combine with bridging hydroxide ions, which take up the coordination sites that would otherwise be occupied by the bridging peroxo group of the dioxygen complex.[10] The bridging groups and the basic nitrogen donor groups of the dioxygen complex of bisdien–Co(II) initially formed account for only five of the required six coordinations of the metal ion, which in the dioxygen complex may be considered to have the properties of Co(III). That the sixth position is probably occupied by water molecules is indicated by the facile dissociation of two protons from the dioxygen complex, resulting in the successive formation of a dihydroxo– and a trihydroxo–dioxygen complex at higher pH. The additional hydroxide ions are assumed to be monodentate in this system. The fact that these hydroxo ligands are not as effective in excluding the peroxo bridge derived from dioxygen may result from the greater flexibility of the macrocyclic ligand as compared to that of the macrobicyclic bistren cryptand.

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Registry No. **1**, 43090-52-4; oxygen, 7782-44-7; ethylenediamine, 107-15-3; imidazole, 288-32-4.

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