appears that the six-membered chelate rings may be destabilizing this complex in a manner analogous to that in which the cobalt–dioxygen complex of PYDPT is destabilized, but it is also possible that the use of O donors in place of N donors may be responsible for the structural features cited.

Calorimetric studies of the oxygenation of cobaltous PYDIEN and PYDPT and of the cobaltous complexes of other similar ligands are presently being undertaken to provide further information about the thermodynamics of oxygenation in solution and the factors influencing the metal–dioxygen affinities in complexes of this type. Studies of the oxygenation equilibria for cobaltous complexes of terdentate and tetradentate ligands which form six-membered chelate rings with cobalt are planned. Such studies will indicate whether the effect of chelate ring size on the stability of dioxygen complexes is a general phenomenon or one peculiar to complexes containing pentadentate ligands.

Acknowledgment. This work was supported by Grant No. A-259 from the Robert A. Welch Foundation. The authors thank Drs. Jan Troup and Mike Extine of the Molecular Structure Corp. for their advice and assistance.

Registry No. $[\mathrm{Co(PYDIEN)}]_2\mathrm{O}_2\mathrm{I}_4$, 71230-49-4; **1**, 58214-73-6; 2-pyridinecarboxaldehyde, 1121-60-4; bis(2-aminoethyl)amine, 111-40-0.

Supplementary Material Available: A table of observed and calculated structure factors (10 pages). Ordering information is given on any current masthead page.

References and Notes

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New Multidentate Ligands. 18. Synthesis of 1,4-Bis(bis(2-aminoethyl)aminomethyl)benzene: Binuclear Chelating Tendencies and Mixed-Ligand Binuclear Chelate Formation

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Received October 13, 1978

The synthesis of 1,4-bis(bis(2-aminoethyl)aminomethyl)benzene hexahydrochloride (PXBDE) and the aqueous solution equilibria of this new hexadentate ligand with Cu(II), Ni(II), Co(II), and Zn(II) in both the presence and the absence of auxiliary bidentate ligands are described. At 25 °C and 0.10 M ionic strength, the protonation constants for PXBDE are 10.06, 9.71, 9.11, 8.57, 1.8, and 1.2 log units. The log K values of the 1:1 metal chelate stability constants ($K = [\mathrm{MH_2L}]/[\mathrm{M}][\mathrm{H_2L}]$) are 13.21, 9.20, 6.84, and 7.19 with the above metals, respectively. For some metal ions at higher pH less protonated forms of the metal chelate, MHL^{3+} and ML^{2+}, are also found. ML^{2+} reacts with excess metal ion to form a binuclear complex ($\mathrm{M_2L}^{4+}$), while in <0.001 M solutions excess PXBDE fails to form a 1:2 metal–ligand complex with any of the above metal ions. PXBDE was found to form mixed-ligand complexes in the presence of metal ions and such bidentate ligands as ethylenediamine and glycine. The logarithms of the equilibrium formation constants for the most fully coordinated glycine species, $\beta = [\mathrm{M_2L'_2L}]/[\mathrm{M}]^2[\mathrm{L'}]^2[\mathrm{L}]$, where L′ = glycine, L = PXBDE, and M = Cu(II), Ni(II), Co(II), or Zn(II), are 37.96, 30.16, 23.38, and 25.56, respectively. Similarly when L′ = ethylenediamine, the corresponding constants are 40.18, 31.68, 23.32, and 27.08. The probable arrangements of the coordination sites in the complexes studied and possible applications of the mixed-ligand systems are discussed.

Introduction

Ligands with two multidentate moieties separated by a rigid bridge such as *p*- or *m*-xylene form binuclear complexes in which the metal ions are held apart at a sufficient distance such that the two groups of donor atoms could not coordinate to the same metal ion, and the binuclear complexes would thus be stable relative to other types of coordinate bond arrangement. However, by appropriate adjustment of the size of the ligand backbone, the metal–metal distance would be rendered suitable for binding a small molecule or ion simultaneously to both coordinated metal centers. Binuclear complexes of "wishbone" ligands of this type may provide interesting models for studying catalytic reactions of biological systems in which concerted effects of both metal ions are involved. The first ligand to be synthesized with this idea in mind, *P,P,P′,P′*-tetrakis(2-diphenylphosphinoethyl)-α,α'-diphospha-*p*-xylene, was reported by Taqui Khan and Martell[1] and was shown to preferentially form binuclear chelates of Ru(II), Rh(I), and Ir(I). A similar bis-tetradentate ligand,[2] containing amino oxygen ether and thioether donor groups,

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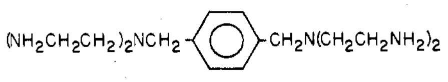
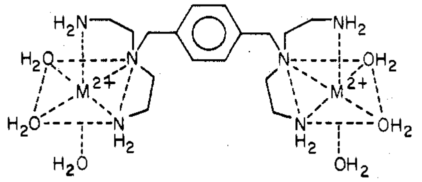
has the same type of *p*-xylene framework and was labeled an "earmuff" type ligand. The solid binuclear Cu(I) complex was reported by Osborn et al.[2] to combine reversibly with dioxygen. Recently, the reactions of a mixed tertiary-phosphine–tertiary-arsine ligand having the same *p*-xylene backbone were described by Taqui Khan et al.[3]

In this paper the synthesis and metal complex equilibria of the bis-terdentate hexaamine 1,4-bis(bis(2-aminoethyl)aminomethyl)benzene (PXBDE), I, are described. The terdentate moieties of the ligand are spaced sufficiently far apart to require coordination with two metal ions as indicated in II, rather than with a single metal ion. It is well-known that analogous hexaamines such as (ethylenedinitrilo)tetrakis(2-ethylamine),[4] PENTEN (III), and (trimethylenedinitrilo)tetrakis(2-ethylamine),[5] PBTRIEN (IV), with flexible two- and three-carbon bridges between the terdentate moieties, form almost exclusively mononuclear hexacoordinated complexes with metal ions of coordination number 6. Clearly then, ligands possessing short flexible bridges between sets of coordination sites do not constitute effective ligands for the formation of metal chelates that would be useful for modeling catalytic activity of natural systems in which two metal ions may undergo concerted participation in the mechanism of the reaction. This paper describes the coordination behavior of the new bis(triamine) PXBDE, which will subsequently be employed for the synthesis of binuclear species of interest as models for metalloenzyme systems.



I, PXBDE



II (probable coordinate bonding in Ni_2L^{4+} and Co_2L^{4+})

$(H_2NCH_2CH_2)_2NCH_2CH_2N(CH_2CH_2NH_2)_2$

III, PENTEN

$(H_2NCH_2CH_2)_2NCH_2CH_2CH_2N(CH_2CH_2NH_2)_2$

IV, PBTRIEN

Experimental Section

Ligand Synthesis. Diphthaloyldiethylenetriamine. A mixture of diethylenetriamine (10.3 g, 0.10 mol) and phthalic anhydride (33.2 g, 0.20 mol) in 160 g of glacial acetic acid was refluxed for 1 h. Solvent was removed on a rotary evaporator using a boiling water bath and was replaced with 160 g of hot ethanol (95%) with stirring until a solid appeared. The product was collected and washed with cold ethanol: yield 142 g (78%); mp 182–183 °C.

***α,α′*-Bis(diphthaloyldiethylenetriamino)-*p*-xylene.** *α,α′*-Dibromo-*p*-xylene (13.2 g, 0.05 mol), diphthaloyldiethylenetriamine (42.7 g, 0.12 mol), and Na_2CO_3 (0.11 mol) were refluxed in 350 mL of DMF for 20 h. The solution was filtered hot and overnight yielded a pale yellow solid which was collected and dried under vacuum: yield 40%; mp 227–231 °C dec.

1,4-Bis(bis(2-aminoethyl)aminomethyl)benzene (I). A modified Gabriel method was employed in the hydrolysis of the phthalic derivative obtained above. *α,α′*-Bis(diphthaloyldiethylenetriamino)-*p*-xylene (23.5 g, 0.050 mol) and 95% hydrazine (0.060 mol) were refluxed in 200 mL of ethanol for 10 h. The solution was saturated with HCl, refluxed for 1 h, and filtered at room temperature. Insoluble products and inorganic salts were removed after the volume of the solvent was reduced on a rotary evaporator. Ethanol was then added to the filtrate, and again the solution was resaturated with HCl. The product was collected after the filtrate was allowed to crystallize overnight. The pure ligand hexahydrochloride was obtained by recrystallization from ethanol and a minimum of water. NMR spectra (D_2O) showed three peaks: 2.62 (a broad singlet), 3.64 (singlet), 7.26 ppm (singlet) in the ratio of 4:1:1. The yield was 5.0 g, 20.0%. Anal. Calcd for $C_{16}H_{38}N_6Cl_6{\cdot}H_2O$: C, 35.23; H, 6.69; N, 15.14; Cl, 39.38. Found: C, 35.53; H, 7.34; N, 15.41; Cl, 39.03.

Reagents. 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 previously standardized EDTA[6] in the presence of appropriate indicators. Carbonate-free solutions of 0.1000 M KOH were prepared from Dilut-it (R) ampules and standardized with potassium acid phthalate. Glycine was purified by recrystallization from aqueous ethanol while ethylenediamine dihydrochloride was obtained as reagent grade material and was used directly. Potassium nitrate, used as supporting electrolyte, was also obtained as reagent grade material.

Potentiometric Equilibrium Measurements. Potentiometric measurements of PXBDE in the absence and 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 by the addition of KNO_3. Typical concentrations of the experimental solutions were either 0.0010 or 0.0020 M in ligand. For all binary systems, equilibrium measurements were made on solutions containing 1:1, 2:1, and 1:2 molar ratios of metal ion to PXBDE. Ternary systems contained metal, PXBDE, and auxiliary ligand in the respective molar ratios 1:1:1, 2:1:1, and 2:1:2. When precipitation became a problem during potentiometric titration, the nature of the precipitate was deduced from the following elemental analyses of precipitates from the 1:1 and 2:1 metal–ligand systems. Anal. Calcd for $[Cu(C_{16}N_6H_{32}){\cdot}2NO_3]_x$: C, 38.75; N, 22.60; H, 6.45. Found (1:1 system): C, 38.85; N, 22.27; H, 6.34. Found (2:1 system): C, 38.68; N, 21.87; H, 6.31. Calcd for $[Co(C_{16}N_6H_{32}){\cdot}2NO_3{\cdot}2.5H_2O]_x$: C, 35.83; N, 20.90; H, 6.90. Found (1:1 system): C, 35.50; N, 20.47; H, 5.80. Found (2:1 system): C, 36.52; N, 21.21; H, 5.95. Calcd for $[Ni(C_{16}H_6N_{32}){\cdot}2NO_3{\cdot}1.5H_2O]_x$: C, 37.09; N, 21.63; H, 6.76. Found (1:1 system): C, 37.23; N, 20.96; H, 6.26. Found (2:1 system): C, 37.17; N, 21.84; H, 6.06. Calcd for $[Zn(C_{16}N_6H_{32}){\cdot}2NO_3]_x$: C, 38.60; N, 22.52; H, 6.43. Found (1:1 system): C, 39.43; N, 21.50; H, 6.28. Found (2:1 system): C, 41.46; N, 21.70; H, 6.21.

Computations. The proton association constants for PXBDE were determined by using the program PKAS.[7] Preliminary 1:1 metal to PXBDE interaction constants K_{ML} were obtained through the algebraic solution of appropriate mass-balance and charge-balance equations evaluated at each equilibrium point of the formation curves. A detailed refinement of the preliminary values was completed with program BEST, written in these laboratories. The input for BEST consists of entering the components and their concentrations, the initial estimates of the equilibrium constant for each species thought to be present in terms of these solution components, and finally the potentiometric equilibrium data determined experimentally. 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 effect a minimization in the difference between the calculated and observed values of $-\log [H^+]$. Error estimates reported in this work are a measure of pH fit over the entire equilibrium curve. No attempt is made to "invent" species for the purpose of a better fit to experimental curves. Species are systematically introduced according to established chemical principles.

Results

Metal-Free PXBDE. In the absence of added metal ions, the potentiometric equilibrium curve of PXBDE hexahydrochloride, shown in Figure 1, is seen to possess a sharp inflection at $a = 2$, where a is moles of base per mole of ligand, followed by an extensive buffer region from $a = 2$ to $a = 6$. The first inflection corresponds to the neutralization of the two most acidic protons which are nearly completely dissociated in the aqueous solution. All six deprotonation steps were found to occur in a pH range that was suitable for the protonation constants to be calculated directly from the potentiometric data. The log values obtained at 25 °C, $\mu = 0.100$

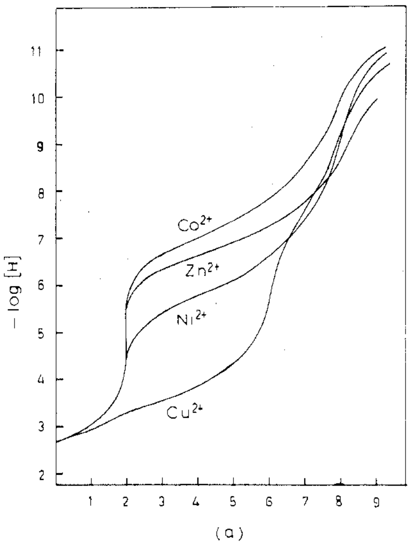


Figure 1. Potentiometric equilibrium curves of 1:1 M–PXBDE·6HCl as a function of added base measured at 25 °C, $\mu = 0.100$ M (KNO_3). In each case $T_{M^{2+}} = T_L = 1.00 \times 10^{-3}$ M. a = mol of base/mol of PXBDE.

Table I. Protonation Constants of PXBDE and Analogous Compounds

	PXBDE[a]	PENTEN[b]	PBTRIEN[c]	DIEN
$\log K^H_1$	10.06	10.08	10.24	9.84
$\log K^H_2$	9.71	9.58	9.56	
$\log K^H_3$	9.11	8.99	9.18	9.02
$\log K^H_4$	8.57	8.42	8.44	
$\log K^H_5$	1.8	1.3	2.5	4.02
$\log K^H_6$	1.2			

[a] This work; 25.0 °C, $\mu = 0.1$ (KNO_3), $\sigma_{fit} = 0.008$ log unit. [b] Reference 4. [c] Reference 5.

M, defined by eq 1 and 2, are 10.06, 9.71, 9.11, 8.57, 1.8, and 1.2, $\sigma = 0.008$. These constants are listed in Table I with values of analogous compounds for comparison.

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

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

Metal Ion–PXBDE Systems. The potentiometric equilibrium curves in Figure 1 for a 1:1 molar ratio of ligand to metal ion indicate that Ni(II), Co(II), and Zn(II) interact with PXBDE only after two protons of the ligand have been neutralized, while the Cu(II) formation curve begins at lower pH. At $a = 4$ the Cu–PXBDE complex is completely formed and is assigned the formula CuH_2L^{2+}. Cobalt and nickel systems cannot be studied completely owing to precipitation of the polymeric $(ML)_x^{xn+}$ material at $a = 4$ and 3.5, respectively, as indicated in Figure 1. Beyond $a = 4$ the data indicate deprotonation reactions of the MH_2L^{4+} complexes, leading to the formation of completely deprotonated species, ML^{2+}. The buffer region in the Zn(II) curve extends from $a = 2$ to $a = 6$; however, beyond $a = 5$ (pH 8.5) metal chelate hydrolysis probably takes place. The mathematical model which explains the observed 1:1 curves shown in Figure 1 can be summarized in terms of the equilibrium equations and corresponding formation constants shown in eq 3–5. The

$$M^{2+} + H_2L^{2+} \rightleftharpoons MH_2L^{4+}$$

$$K^M{}_{MH_2L} = [MH_2L^{4+}]/[M^{2+}][H_2L^{2+}] \tag{3}$$

$$M^{2+} + 2H^+ + L \rightleftharpoons MH_2L^{4+}$$

$$\beta_{MH_2L} = [MH_2L^{4+}]/[M^{2+}][H^+]^2[L] \tag{4}$$

$$M^{2+} + H^+ + L \rightleftharpoons MHL^{3+}$$

$$\beta_{MHL} = [MHL^{3+}]/[M^{2+}][H^+][L] \tag{5}$$

formation constant calculations which were carried out as discussed above yielded the values which are listed in Table II.

Mathematical analysis of potentiometric data obtained for two ligands to one metal ion system indicated that no significant concentration of ML_2 complex formed. The experimental curves were reproduced exactly by employing the equilibrium model shown in eq 3–5 together with the values of the equilibrium constants obtained from the 1:1 data.

For the two metal to one ligand equilibrium systems containing a 2:1 ratio of metal ion to ligand, only the Cu(II) and Zn(II) solutions failed to give precipitates of the polymeric chelates, which were also formed in the 1:1 systems. The Cu(II) 2:1 curve (not shown) is markedly lowered, indicating the formation of Cu_2L species is virtually complete at $-\log [H^+] = 5$. The Zn(II) 2:1 curve is also quite low, indicating some Zn_2L formation, while Co(II) and Ni(II) exhibited the formation of insoluble polymeric species.

The additional relationship found necessary to treat the 2:1 metal to ligand solution equilibria is shown as eq 6. The values

$$ML^{2+} + M^{2+} \rightleftharpoons M_2L^{4+}$$

$$K^M{}_{M_2L} = \frac{[M_2L^{4+}]}{[ML^{2+}][M^{2+}]} \qquad \beta_{M_2L} = \frac{[M_2L^{4+}]}{[M^{2+}]^2[L]} \tag{6}$$

calculated for these 2:1 metal:ligand stability constants by using the 1:1 chelate formation and deprotonation constants obtained from the 1:1 systems are given in Table II and are discussed in the next section.

Mixed-Ligand Complexes. The formation of ternary complexes in systems containing 2:1:2 molar ratios of either glycine or ethylenediamine to PXBDE to metal ion renders all metal chelates soluble throughout the pH range studied. The potentiometric equilibrium curves for the glycine–PXBDE systems are shown in Figure 2. The Cu(II) curve possesses an inflection at $a = 6$. The buffer region which follows and culminates with an inflection at $a = 8$ corresponds to the formation of the copper(II) mixed-ligand complex. The Co(II), Ni(II), and Zn(II) curves possess continuous buffer regions extending from $a = 2$ to $a = 8$. Therefore, for these metal ions the successive formation of complex species is an overlapping process. The inflections at $a = 8$ (Figure 2) signify the coordination of PXBDE and glycine with the metal ion to be complete.

Table II. log Stability Constants for Divalent Metal Ions with PXBDE at 25.0 °C, $\mu = 0.100$ M (KNO_3)

	K_{ML}	β_{MHL}[a]	β_{MH_2L}[b]	$K^M{}_{MH_2L}$[c]	β_{M_2L}[d]	$\beta_{M_2L(OH)}$[e]	$\beta_{M_2L(OH)_2}$
Cu	15.53 (±0.03)	24.52 (±0.03)	32.98 (±0.02)	13.21 (±0.02)	27.78 (±0.02)	33.22 (±0.05)	37.86 (±0.05)
Co		18.88 (±0.04)	26.6 (±0.02)	6.84 (±0.02)	14.58 (±0.04)		
Ni		20.27 (±0.04)	28.97 (±0.03)	9.20 (±0.03)	19.77 (±0.04)		
Zn	10.05 (±0.03)	19.18 (±0.03)	26.96 (±0.03)	7.19 (±0.03)	16.14 (±0.03)		

[a] $\beta_{MHL} = [MHL]/[M][H][L]$. [b] $\beta_{MH_2L} = [MH_2L]/[M][L][H]^2$. [c] $K_{MH_2L}{}^M = [MH_2L]/[M][H_2L]$. [d] $\beta_{M_2L} = [M_2L]/[M]^2[L]$. [e] $\beta_{M_2L(OH)} = [M_2L(OH)]/[M]^2[L][OH]$.

Table III. log Stability Constants for Cu, Ni, Co, and Zn with PXBDE and Glycine or EN at 25 °C, $\mu = 0.100$ M (KNO_3)

	glycine (L′)				EN (L′)			
	$\beta_{M_2LL'_2}$	$K^{L'}{}_{M_2LL'}$	$K^{L'}{}_{M_2LL'_2}$	$K_{ML'}$	$\beta_{M_2LL'_2}$	$K^{L'}{}_{M_2LL'}$	$K^{L'}{}_{M_2LL'_2}$	$K_{ML'}$
Cu	37.96	5.31 (±0.03)	4.87 (±0.03)	8.15	40.18	6.72 (±0.03)	5.68 (±0.03)	10.52
Co	23.38	4.90 (±0.03)	3.90 (±0.03)	4.64	23.32	4.52 (±0.03)	4.22 (±0.03)	5.38
Ni	30.16	5.58 (±0.04)	4.81 (±0.04)	5.78	31.68	6.31 (±0.04)	5.60 (±0.04)	7.45
Zn	25.56	5.05 (±0.05	4.65 (±0.05)	4.98	27.08	5.63 (±0.04)	5.31 (±0.04)	5.70

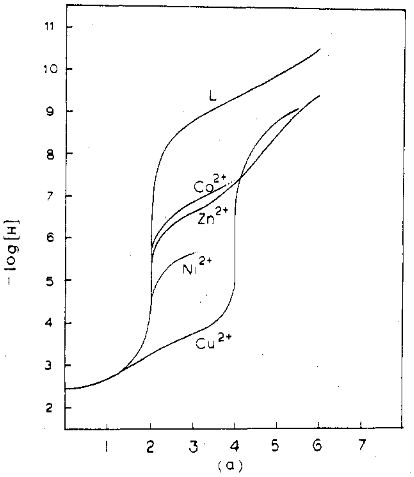


Figure 2. Potentiometric equilibrium curves of 2:2:1 M–glycine–PXBDE·6HCl as a function of added standard alkali measured at 25 °C, $\mu = 0.100$ M (KNO_3). In each case $T_{M^{2+}} = T_{glycine} = 2T_{PXBDE} = 2.00 \times 10^{-3}$ M. a = mol of base/mol of PXBDE.

The mixed-ligand equilibrium curves of PXBDE and ethylenediamine with metal ions are generally more depressed in pH than those shown for glycine in Figure 2. Mixed-ligand formation constants were calculated for both systems with the appropriate ligand protonation and chelate formation constants of glycine and ethylenediamine taken from the literature.[8] As an added check, the protonation constants as well as chelate formation constants were measured for glycine, ethylenediamine, and the appropriate metal ions. The results of these calculations are summarized in Table III. The appropriate relationships for mixed-ligand formation are listed in eq 7–10, where L = PXBDE and L′ = glycine or ethylenediamine.

$$2M + L + L' \rightleftharpoons M_2LL'$$

$$\beta_{M_2L'L} = [M_2L'L]/[M]^2[L'][L] \qquad (7)$$

$$2M + L + 2L' \rightleftharpoons M_2L'_2L$$

$$\beta_{M_2L'_2L} = [M_2L'_2L]/[M]^2[L']^2[L] \qquad (8)$$

$$M_2L + L' \rightleftharpoons M_2LL'$$

$$K^{L'}{}_{M_2LL'} = [M_2LL']/[M_2L][L'] \qquad (9)$$

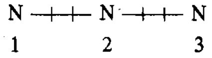
$$M_2LL' + L' \rightleftharpoons M_2LL'_2$$

$$K^{L'}{}_{M_2LL'_2} = [M_2LL'_2]/[M_2LL'][L'] \qquad (10)$$

Discussion

Ligand Protonation Constants. The basicities of the ligand donor groups may be discussed by comparison with the analogous polyamines DIEN (diethylenetriamine), PENTEN, and PBDIEN. The successive protonation steps in DIEN follow the order in Chart I. Step 1 gives rise to a species of composition HL^+ with two microspecies. End protonations probably dominate since they are statistically favored. Coulombic repulsion requires that the predominant H_2L^{2+} species have protons on only the terminal nitrogen donor groups. This charge distribution greatly reduces the protonation tendency in step 3 where the third proton is forced to sandwich between two terminal ammonium groups. These considerations are reflected quantitatively in the relative magnitudes of the protonation constants of DIEN, $10^{9.84}$, $10^{9.02}$, and $10^{4.02}$.

Chart I



step	protonation site
1	position 1, 2, or 3
2	positions 1 and 3
3	positions 1, 2, and 3

The ligand PXBDE, I, contains two widely separated DIEN molecules. Thus the stepwise protonation of PXBDE can be envisioned as proceeding through the successive formation of the protonated species HL^+ to H_4L^{4+}, none of whose microspecies possess structures for which Coulombic repulsion is a dominant consideration. Hence the successive protonation constants (Table I) monotonically decrease while reflecting a general buildup of widely separated positive charge until the fifth and sixth steps, where charge repulsion becomes not only inevitable but also dominant in determining the low basicity of the two central nitrogen atoms. For comparison, the successive values for the protonation constants[8] for PENTEN and PBTRIEN may also be rationalized in a similar manner.

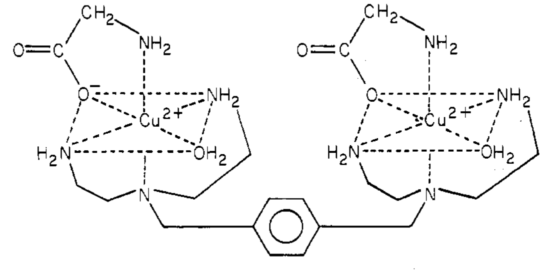
Metal Chelate Stability Constants. When compared with hexadentate ligands possessing short, flexible bridges such as found in PENTEN and PTETRAEN, the 1:1 metal chelate stability constants of PXBDE are much lower. The *p*-xylene bridge in PXBDE contrasted with the ethylene and propylene bridges in PENTEN and PBTRIEN precludes the participation of all six nitrogens in 1:1 chelation and hence is responsible for the observed lower metal chelate stability constants. In the 1:1 complex, PXBDE acts as a terdentate ligand while the "uncoordinated" end is still protonated. The lowering of the basicity of the uncoordinated end by the metal ion is not expected to be very great because of the large intergroup distance required by the α,α'-xylene bridge.

The ligand is also very well suited to the formation of 1:1 polymers with hexacoordinate metal ions. Since only one of the diethylenetriamine groups of the ligand can coordinate to a given metal ion, three coordination sites remain open on the metal ion which can then react with other partially coordinated ligand molecules, resulting in the formation of high molecular weight polymers. Thus for the 1:1 systems, as more base was added after the initial formation of the MH_2L^{2+} complex, coordination of the deprotonated remote amino groups of one chelate molecule with the metal ion of another chelate molecule results in the precipitation of polynuclear high molecular weight Co(II), Ni(II), and Zn(II) chelates at $a = 4$, $a = 3.5$, and $a \simeq 6$, respectively. In the first two systems, the concentration of the fully deprotonated 1:1 chelate, ML, was always lower than that of other major species by 4–5 orders of magnitude. Whenever the concentration of ML exceeded a certain value, it then proceeded to form insoluble polymers. The 1:1 formation constants for Co(II) and Ni(II) are best expressed in terms of the protonated chelate MH_2L, a major species in all metal systems studied. A possible explanation for the reduced polymerization tendency in the case of Zn–PXBDE complex is the formation of a tetrahedral ion[9,10] of the type $[Zn(H_2O)H_2L]^{4+}$, where L = PXBDE.

In systems where two metal ions are equilibrated with one ligand, Co(II) and Ni(II) also seem to form the same polymers as those formed in the 1:1 systems. Apparently the solubilities of these polynuclear polymeric species are so low that precipitate formation eventually drives the equilibrium toward complete dissociation of M_2L. Hence for Co(II) and Ni(II) the 2:1 metal to ligand stability constant can be calculated from only the initial portion of the buffer region of the potentiometric curves.

The formation of chelates containing a 2:1 ligand to metal ratio could not be detected, and only 1:1 chelates were found in systems containing 2:1 ratios of reactants. The data indicate that half of the total ligand interacts with metal ions forming the 1:1 complex. Since the chelate protonation constants are lower than those of the ligand, deprotonation will take place in the chelate before it can occur in the uncoordinated ligand. Thus as base is added, polymerization develops before the formation of the ML_2 type complex can be observed.

Mixed-Ligand Complexes. Each end of PXBDE can bind to the Cu(II) ion in such a fashion that the three nitrogens about the metal may be in the equatorial plane. The addition of an auxiliary bidentate ligand would result in a structure in which the fourth coordination site in the equatorial as well as the fifth in the axial position would become occupied. Cu(II) complexes usually have "distorted" octahedral configurations,[11] in which the bonds in the axial position are lengthened and considerably weakened. Thus, binding of glycine and ethylenediamine to the PXBDE dicopper(II) chelate probably occurs through the formation of a chelate ring between an axial position and the remaining in-plane coordination site (V). The coordination geometries of the mixed-ligand complexes with Ni(II), Co(II), and Zn(II) in solution are not distinguishable with the data presently available and may be similar to that suggested for Cu(II) or a mixture of several possible arrangements of primary and secondary ligand donor groups.



V (probable coordinate bonding in a mixed-ligand binuclear PXBDE complex)

With the program described in the computation section, it was possible to calculate the overall stability constants of the mixed-ligand systems. After K_{ML} and K_{M_2L} were estimated from the 1:1, 2:1, and mixed-ligand systems, the stepwise stability constants $K^{L'}_{M_2L'L}$ and $K^{L'}_{M_2L'_2L}$ were obtained and are shown in Table III. When compared with the second formation constants $[ML'_2]/[ML'][L']$ of glycine, the metal chelate formation constants, $K^{L'}_{M_2L'L}$ and $K^{L'}_{M_2L'_2L}$, are relatively large. However, large mixed-ligand constants have also been reported for the 2,2′-bipyridyl system.[12,13]

Some preliminary work has also been done on mixed-metal chelates of PXBDE. Thus pairs of metal ions Cu(II)–Co(II) and Cu(II)–Ni(II) were equilibrated with PXBDE in the ratio of 1:1:1 and were studied as a function of $-\log [H^+]$. There was an inflection at $a = 4$, which demonstrated the complete formation of CuH_2L, followed by a buffer region from $a = 4$ to $a = 6$, which corresponded to the deprotonation reaction resulting from formation of a mixed-metal complex. No precipitates were observed. The magnitudes of the mixed-metal constants $K_{MLM'}$, defined by eq 11, are similar to the

$$ML + M' \rightleftharpoons MLM'$$

$$K^{M'}_{MLM'} = [MLM']/[ML][M'] \qquad (11)$$

magnitudes of the constants $K^{M}_{MH_2L}$ obtained from the 2:1 metal to ligand ratio and mixed-ligand systems. The metal ion on one end of the PXBDE ligand seems to have little influence on the coordination behavior of another metal ion on the other end. For example, when M = Cu(II) and M′ = Co(II), $\log K^{M'}_{MLM'} = 6.32$, and for M = Cu(II) and M′ = Ni(II), $\log K^{M'}_{MLM'} = 8.75$. These values are approximately what would be expected for $\log K^{M}_{M_2L}$ when M = Co(II) and Ni(II), respectively.

In the Co(II) mixed-ligand chelate, $Co_2LL'_2{}^{4+}$, each Co(II) ion is coordinated to a bidentate ligand and a diethylenetriamine group of PXBDE, leaving an octahedral coordination site open (i.e., aquated). Molecular models show that the space between the two Co(II) ions is sufficient to accommodate a diatomic bridging group such as a dioxygen molecule. It should be possible for oxygen to react with the mixed-ligand complex in such a fashion that oxygen will replace the two H_2O groups in the open coordination sites and bridge the two Co(II) atoms, thus forming an intramolecular binuclear dioxygen complex. Work is continuing in this laboratory on the formation and properties of these interesting binuclear complexes.

Acknowledgment. This work was supported by a research grant (No. A-259) from the Robert A. Welch Foundation.

Registry No. I·6HCl, 71277-15-1; α,α′-bis(diphthaloyldiethylenetriamino)-*p*-xylene, 71277-16-2; diphthaloyldiethylenetriamine, 63563-83-7; α,α′-dibromo-*p*-xylene, 623-24-5; diethylenetriamine, 111-40-0; phthalic anhydride, 85-44-9; $[Cu(PXBDE)(NO_3)_2]_x$, 71277-66-2; $[Co(PXBDE)(NO_3)_2]_x$, 71277-68-4; $[Ni(PXBDE)(NO_3)_2]_x$, 71277-70-8; $[Zn(PXBDE)(NO_3)_2]_x$, 71277-72-0; PXBDE, 71277-17-3; glycine, 56-40-6; en, 107-15-3; Cu, 7440-50-8; Co, 7440-48-4; Ni, 7440-02-0; Zn, 7440-66-6.

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