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Interactions between Divalent Metal Ions and an Octacoordinate Macrocyclic Ligand

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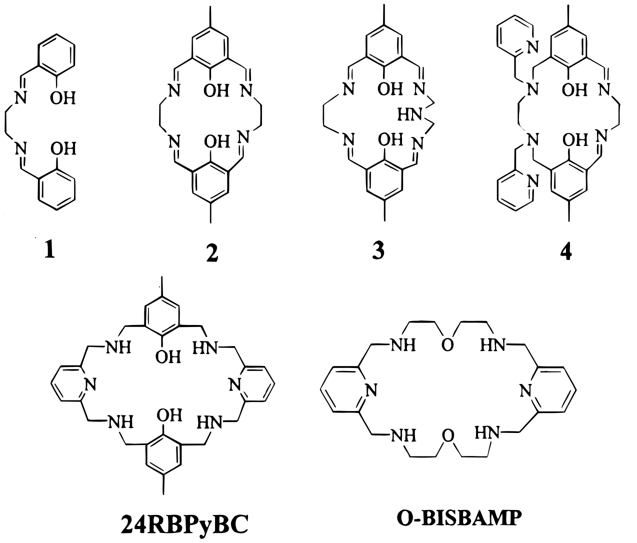
A dinucleating hexaazadiphenol macrocyclic ligand, 15,31-dimethyl-3,11,19,27,33,35-hexaazapentacyclo-$[27.3.1.1.^{5,9}1.^{13,17}1.^{21,25}]$hexatriaconta-5,7,9(33),13,15,17(34),21,23,25(35),29,31,1(36)-dodecaene-34,36-diol (H_2L), forms a number of protonated, neutral, and/or hydroxo mononuclear, homodinuclear, and heterodinuclear complexes with the divalent metal ions Cu^{2+}, Cd^{2+}, Mn^{2+}, and Zn^{2+}, controlled by the stoichiometry of the metal ion and ligand as well as the pH values of the solution. Their stability constants and species distribution as a function of p[H] are determined. The pH potentiometric studies show that the dinuclear complexes are formed via the mononuclear chelates in which two kinds of coordination patterns are observed. One is that the metal ions are complexed by exactly half of coordination sites of the dinucleating macrocycle (N_3O^-), and the other is that the metal ions occupy salen-like sites of the macrocycle ($N_3O_2^{2-}$). In the 2:1 systems (2:1 molar ratio of metal ion to ligand), the mononuclear species predominate in acidic solutions while the dinuclear species predominate in basic solutions, except for the case of copper. The protonated mononuclear complex $[H_2LZn](NO_3)_2\cdot 5H_2O$ forms triclinic crystals, of space group P_1, with $a = 10.7797(12)$ Å, $b = 10.9047(12)$ Å, $c = 17.0176(15)$ Å, $\alpha = 106.857(9)°$, $\beta = 95.822(8)°$, $\gamma = 100.191(9)°$, and $Z = 2$; the neutral heterodinuclear complex $[LZnCdCl_2]\cdot 6H_2O$ forms monoclinic crystals, of space group $C2/c$, with $a = 16.234(5)$ Å, $b = 15.976(9)$ Å, $c = 29.829(11)$ Å, $\alpha = 90°$, $\beta = 90.28(2)°$, $\gamma = 90°$, and $Z = 8$.

Introduction

During the past decade, metal complexes with salen ligands (**1**; see Chart 1), derived from the condensation of salicylaldehyde with a diamine, have been studied extensively in view of their significance as biomimetric catalysts in the process of oxygenation.[1] Recent discoveries of dinuclear cores at the active sites of some metalloproteins have evoked interest in the investigation of multimetallic systems.[2] Dinucleating macrocyclic ligands which are preorganized molecules capable of binding two metal ions in close proximity have received considerable attention.[3] This is particularly true for a family of tetraazadiphenol macrocycles (**2**) relevant to salen, introduced first by Robson et al.,[4] derived from the [2 + 2] template condensation of 2,6-diformyl-*p*-cresol with a diamine in the presence of metal ions. Later, some modifications were made to the tetraimine entity with different lateral chains.[5] Okawa et al. have developed a class of macrocycles (**3**) having unsymmetrical compartments with inequivalent coordination sites by stepwise condensation reactions,[6] and Bosnich et al. have

Chart 1



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[1] (a) Konsler, R. G.; Karl, J.; Jacobsen, E. N. *J. Am. Chem. Soc.* **1998**, *120*, 10780. (b) Wei, P. R.; Atwood, D. A. *Inorg. Chem.* **1997**, *36*, 4060. (c) Kolb, H. C.; Vannieuvvenhze, M. S.; Sharpless, K. B. *Chem. Rev.* **1994**, *94*, 2483. (d) Schurig, V.; Betschinger, F. *Chem. Rev.* **1992**, *92*, 873.

[2] (a) Than, R.; Feldmann, A. A.; Krebs, B. *Coord. Chem. Rev.* **1999**, *182*, 211. (b) Strater, N.; Klabunde, T.; Tucker, P.; Witzel, H.; Krebs, B. *Science* **1995**, *268*, 1489. (c) Vincent, J. B.; Olivierlilley, G. L.; Averill, B. A. *Chem. Rev.* **1990**, *90*, 1447.

[3] (a) Komaei, S. A.; van Albada, G. A.; Haasnoot, J. G.; Kooijman, H.; Spek, A. L.; Reedijk, J. *Inorg. Chim. Acta* **1999**, *286*, 24. (b) Yamami, M.; Furutachi, H.; Yokoyama, T.; Okawa, H. *Inorg. Chem.* **1998**, *37*, 6832. (c) Vanveggel, F. C. J. M.; Verboom, W.; Reinhoudt, D. N. *Chem. Rev.* **1994**, *94*, 279. (d) Nation, D. A.; Martell, A. E.; Carroll, R. I.; Clearfield, A. *Inorg. Chem.* **1996**, *35*, 7246. (e) Lu, Q.; Reibenspies, J. H.; Martell, A. E.; Motekaitis, R. J. *Inorg. Chem.* **1996**, *35*, 7462. (f) Lu, Q.; Reibenspies, J. H.; Martell, A. E.; Motekaitis, R. J. *Inorg. Chem.* **1996**, *35*, 2630.

[4] (a) Pilkington, N. H.; Robson, R. *Aust. J. Chem.* **1970**, *23*, 2225. (b) Gagne, R. R.; Spiro, C. L.; Smith, T. J.; Hamamm, C. A.; Thies, W. R.; Shiemke, A. K. *J. Am. Chem. Soc.* **1981**, *103*, 4073.

[5] (a) Atkins, A. J.; Black, D.; Blake, A. J.; Marin-Bacerra, A.; Parsons, S.; Ruiz-Ramirez, L.; Schröder, M. *J. Chem. Soc., Chem. Commun.* **1996**, 457. (b) Thompson, L. K.; Mandal, S. K.; Tandon, S. S.; Bridson, J. N.; Park, M. K. *Inorg. Chem.* **1996**, *35*, 3117. (c) Matthews, K. D.; Kahwa, I. A.; Williams, D. J. *Inorg. Chem.* **1994**, *33*, 1382. (d) Aguiari, A.; Bullita, E.; Casellato, U.; Guerriero, P.; Tamburini, S.; Vigato, P. A. *Inorg. Chim. Acta* **1992**, *202*, 157. (e) Chang, H. R.; Larsen, S. K.; Boyd, P. D. W.; Pierpont, C. C.; Hendrickson, D. N. *J. Am. Chem. Soc.* **1988**, *110*, 4565.

[6] (a) Furutachi, H.; Ishida, A.; Miyasaka, H.; Fukita, N.; Ohba, M.; Okawa, H.; Koikawa, M. *J. Chem. Soc., Dalton Trans.* **1999**, 367. (b) Okawa, H.; Furutachi, H.; Fenton, D. E. *Coord. Chem. Rev.* **1998**, *174*, 51 and references therein.

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introduced auxiliary donating groups into the macrocycle as pendant arms (**4**).[7]

We have reported the synthesis of a 24-membered Schiff-base hexaazadiphenol macrocycle containing pyridyl groups from the direct condensation of diformylpyridine with bis(aminomethyl)-*p*-cresol, as well as its reduced form 24RBPyBC, 15,31-dimethyl-3,11,19,27,33,35-hexaazapentacyclo[27.3.1.1.^{5,9}1.^{13,17}1.^{21,25}]-hexatriaconta-5,7,9(33),13,15,17(34),21,23,25(35),29,31,1(36)-dodecaene-34,36-diol.[8] The incorporation of two pyridyl groups into the tetraaza macrocycle would be expected to result in enhanced affinity and a larger cavity for metal ions. A macrocyclic ligand having a pyridine ring incorporated into its backbone usually has properties notably different from those of its aliphatic nitrogen analogues.[9−11] Thus, detailed studies of the interactions of 24RBPyBC with metal ions are of interest because the coordination properties of the macrocycle may vary widely.

Metal complexes of Schiff-base forms of the polyazadiphenol macrocycle were found to exhibit different properties from those of the corresponding amine forms. For example, a solution of the dinuclear iron(II) complex of **4** was observed to be very stable in air, with no change for 5 days, whereas the corresponding amine complex was extremely sensitive toward oxygen and its yellow solution was oxidized to a deeply colored solution upon exposure to air.[12] Very recently, we reported that the dinuclear iron(II) complex of 24RBPyBC can effectively catalyze the hydroxylation of hydrocarbons with O_2 in the presence of H_2S.[13] Therefore, the amine forms of such macrocycles are worth investigating because of their complexation behavior. However, studies in this regard are relatively limited,[14] mostly concentrating on synthesis.

In this paper, we focus on the formation of a variety of mononuclear, homodinuclear, and heterodinuclear divalent metal complexes of 24RBPyBC in aqueous solution by control of the stoichiometry of the metal ion and ligand as well as p[H] of solution. The pH potentiometric method is utilized successfully to determine formation constants that govern the interactions between metal ions and the ligand and to determine the distribution of species present in solution as a function of p[H]. The X-ray crystal structures of a protonated mononuclear complex of Zn(II) and a heterodinuclear complex of Zn(II) and Cd(II) are also reported. These structures are found to be useful in guiding and confirming interpretations of the potentiometric work.

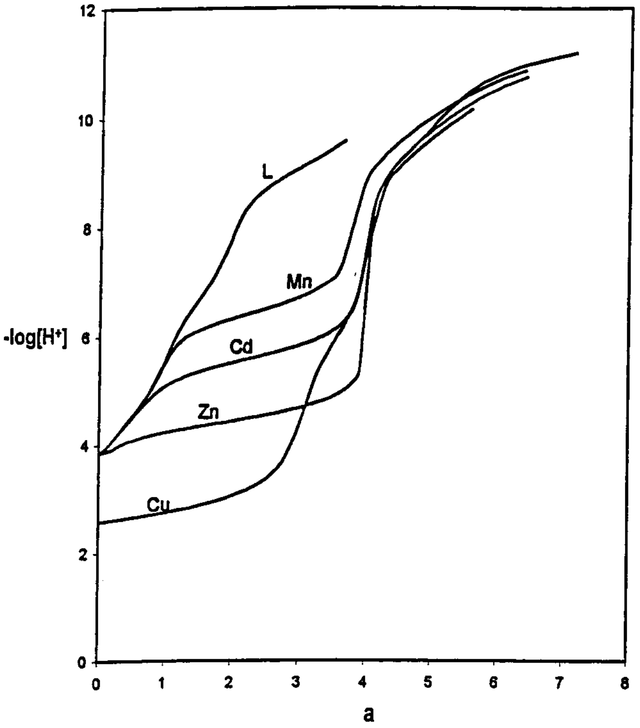

Figure 1. Potentiometric titration curves of the free ligand and the 1:1 molar ratios of H_6L^{4+} with Cu(II), Cd(II), Mn(II), and Zn(II) at 25 °C, $\mu = 0.100$ M (KCl), where *a* is the moles of base added per mole of ligand present.

Results and Discussion

The Ligand. Pyridyl nitrogens in 24RBPyBC were found not to be protonated in low-p[H] aqueous solution (1 mM). Thus, for the ligand, the fully protonated species is designated as H_6L^{4+} and the fully deprotonated species as L^{2-}. log *K* values for six successive stepwise protonation constants of the ligand obtained in this paper, 12.3, 11.5, 9.22, 9.02, 6.69, and 4.47 ($K_n = [H_nL]/[H_{n-1}L][H]$; $n = 1-6$), are in good agreement with previous work.[15] The last four constants, corresponding to four amino groups, were directly measured by pH potentiometric titration, whereas the first two constants, corresponding to two phenolic groups, were determined by the UV−vis spectrophotometric method,[16] rather than direct titration, as p[H] potentiometric measurements are inappropriate for extremely weak acids.

Mononuclear Chelates of Divalent Ions. Titrations of the ligand H_6L^{4+} with Cu(II), Cd(II), Zn(II), and Mn(II) in 1:1 molar ratios were carried out to investigate the mononuclear complexes. Their titration curves are shown in Figure 1. It was found that interactions of the ligand with metal ions in 1:1 ratios led mainly to mononuclear chelates where two kinds of complexation were observed (see Chart 2).

In the titration curves of Zn(II) and Mn(II) systems, the first inflection appeared at $a = 4$ (where *a* is moles of KOH added per mole of ligand present), revealing that the complex initially formed in appreciable concentration is a diprotonated mononuclear chelate (H_2LM^{2+}). It is noteworthy that, in H_2LM^{2+}

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[7] (a) McCollum, D. G.; Bosnich, B. *Inorg. Chim. Acta* **1998**, *270*, 13 and references therein. (b) McCollum, D. G.; Yap, G. P. A.; Rheingold, A. L.; Bosnich, B. *J. Am. Chem. Soc.* **1996**, *118*, 1365.

[8] Wang, Z.; Reibenspies, J.; Martell, A. E. *Inorg. Chem.* **1997**, *36*, 627.

[9] (a) Zhang, X. X.; Bordunov, A. V.; Kou, X.; Dalley, N. K.; Izatt, R. M.; Mangum, J. J.; Li, D.; Bradshaw, J. S.; Hellier, P. C. *Inorg. Chem.* **1997**, *36*, 2586. (b) Kim, W. D.; Hrncir, D. C.; Kiefer, G. E.; Sherry, A. D. *Inorg. Chem.* **1995**, *34*, 2225. (c) Dhont, K. I.; Herman, G. G.; Fabretti, A. C.; Lippens, W.; Goeminne, A. M. *J. Chem. Soc., Dalton Trans.* **1996**, 1753. (d) Rothermel, G. L., Jr.; Miao, L.; Hill, A. L.; Jackels, S. C. *Inorg. Chem.* **1992**, *31*, 4854.

[10] (a) Motekaitis, R. J.; Martell, A. E. *Inorg. Chem.* **1992**, *31*, 5534. (b) Motekaitis, R. J.; Martell, A. E. *Inorg. Chem.* **1991**, *30*, 694.

[11] (a) Motekaitis, R. J.; Utley, W. B.; Martell, A. E. *Inorg. Chim. Acta* **1993**, *212*, 15. (b) Basallote, M. G.; Martell, A. E. *Inorg. Chem.* **1988**, *27*, 4219.

[12] McCollum, D. G.; Yap, G. P. A.; LiableSands, L.; Rheingold, A. L.; Bosnich, B. *Inorg. Chem.* **1997**, *36*, 2230.

[13] Wang, Z.; Martell, A. E.; Motekaitis, R. J. *J. Chem. Soc., Chem. Commun.* **1998**, 1523.

[14] (a) Dutta, S. K.; Werner, R.; Florke, U.; Mohanta, S.; Nanda, K. K.; Haase, W.; Nag, K. *Inorg. Chem.* **1996**, *35*, 2292. (b) Mandal, S. K.; Thompson, L. K.; Nag, K.; Charland, J. P.; Gabe, E. J. *Inorg. Chem.* **1987**, *26*, 1391.

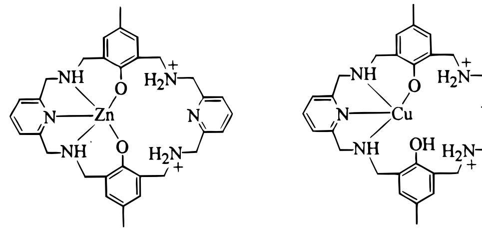
[15] Wang, Z. Ph.D. Dissertation, Texas A&M University, 1997.

[16] Motekaitis, R. J.; Martell, A. E.; Welch, M. J. *Inorg. Chem.* **1990**, *29*, 1463.

[17] McCollum, D. G.; Hall, L.; White, C.; Ostrander, R.; Rheingold, A. L.; Whelan, J.; Bosnich, B. *Inorg. Chem.* **1994**, *33*, 924.

[18] Ohtsuka, S.; Kodera, M.; Motoda, K.; Ohba, M.; Okawa, H. *J. Chem. Soc., Dalton Trans.* **1995**, 2599.

Chart 2



H_2LZn^{2+} **H_3LCu^{3+}**

Table 1. log *K* Values for the Stability Constants of the Mononuclear, Homodinuclear, and Heterodinuclear Complexes of 24RBPyBC[a]

	K_{LM}	K_{HLM}	K_{H_2LM}	K_{H_3LM}	K_{LM_2}	β_{LM_2}	$K_{L(OH)M_2}$	$K_{L(OH)_2M_2}$
Mn	12.27	10.81	9.55		8.54	20.81	11.18	
Cd	15.42	10.09	9.28	5.70	11.17	26.59	10.67	
Zn	18.95	10.69	9.28		11.20	30.15	8.45	10.44
Cu	23.51	11.84	9.20	5.77	21.75	45.26		
Zn−Mn						26.52[b]	10.06[e]	
Zn−Cd						29.97[c]	10.82[f]	
Cu−Cd						35.96[d]	10.91[g]	

[a] Estimated error ±0.04. $K_{LM} = [LM]/[M^{2+}][L^{2-}]$, $K_{HLM} = [HLM^+]/[LM][H^+]$, $K_{H_2LM} = [H_2LM^{2+}]/[HLM^+][H^+]$, $K_{H_3LM} = [H_3LM^{3+}]/[H_2LM^{2+}][H^+]$, $K_{LM_2} = [LM_2^{2+}]/[LM][M^{2+}]$, $\beta_{LM_2} = [LM_2^{2+}]/[L^{2-}][M^{2+}]^2$, $K_{L(OH)M_2} = [LM_2^{2+}]/[H^+][L(OH)M_2^+]$, $K_{L(OH)_2M_2} = [L(OH)M_2^+]/[H^+][L(OH)_2M_2]$. [b] $\beta_{LM_2} = [LZnMn^{2+}]/[L^{2-}][Zn^{2+}][Mn^{2+}]$. [c] $\beta_{LM_2} = [LZnCd^{2+}]/[L^{2-}][Zn^{2+}][Cd^{2+}]$. [d] $\beta_{LM_2} = [LCuCd^{2+}]/[L^{2-}][Cu^{2+}][Cd^{2+}]$. [e] $K_{L(OH)M_2} = [LZnMn^{2+}]/[H^+][LZnMn(OH)^+]$. [f] $K_{L(OH)M_2} = [LZnCd^{2+}]/[H^+][LZnCd(OH)^+]$. [g] $K_{L(OH)M_2} = [LCuCd^{2+}]/[H^+][LCuCd(OH)^+]$.

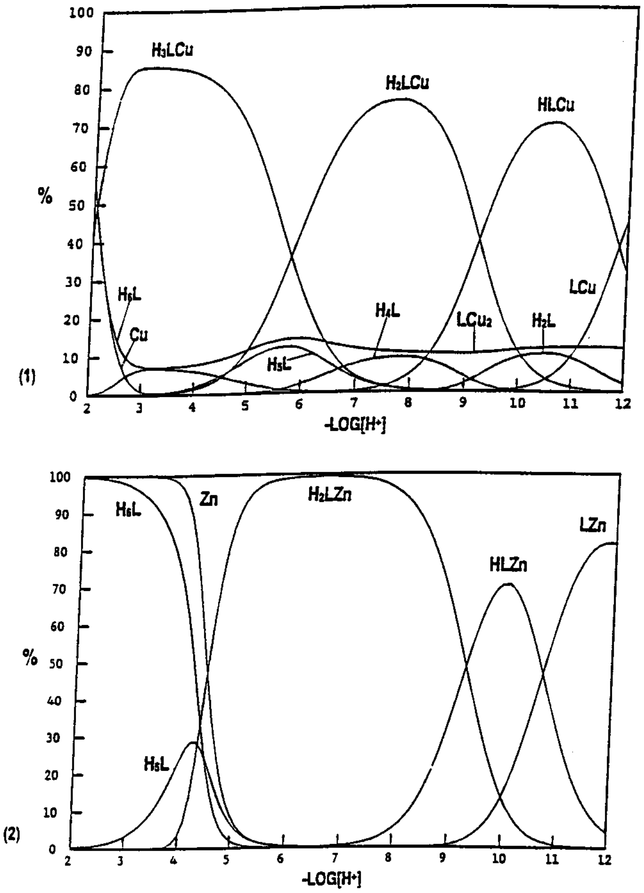


Figure 2. Species distribution diagrams indicating the species present as a function of p[H] in the systems containing 1:1 molar ratios of (1) Cu(II)−H_6L^{4+} and (2) Zn(II)−H_6L^{4+} at 25 °C, $\mu = 0.100$ M (KCl). % = percent of total concentration of ligand (1×10^{-3} M) set at 100%. The minor species (maximum content less than 5%) are omitted for clarity.

species, two protons are attached not to phenolic groups but to amino groups located on one side of the macrocycle. This conclusion is easily deduced from the p[H] profiles of the titrations at *a* = 4−6 having lower p[H] values. Also, the crystal structure of H_2LZn^{2+} confirms it. The sequence of deprotonation for the complexed ligand is different from that for the free ligand.

For the Cu(II) system, the inflection starting at *a* = 3 suggests that the species initially formed is a triprotonated mononuclear chelate H_3LCu^{3+}, where Cu is complexed by half the coordination sites of the macrocycle. For the Cd(II) system, the inflection at *a* = 4 is quite similar to those for the Zn(II) and Mn(II) systems, but mathematical analysis of the titration points reveals that, in addition to the normal H_2LCd^{2+} species, a triprotonated species H_3LCd^{3+} in appreciable amounts (maximum of 21% at p[H] = 5.7) is formed concomitantly and is found to be converted sequentially into LCd_2^{2+} by combination with another Cd(II).

The protonated mononuclear complexes initially formed undergo simple deprotonation reactions at higher p[H].

The stability constants of the mononuclear complexes listed in Table 1 show that the affinity of the ligand for metal ions increases in the order Mn(II) < Cd(II) < Zn(II) < Cu(II). To understand better the magnitude of these stability constants, it may be useful to compare the stability constants with those of a similar hexaaza macrocycle without two phenolic groups, O-BISBAMP (see Chart 1).[11] Comparison of the stability constants of the Cu(II) and Zn(II) complexes of these two ligands (24RBPyBC and O-BISBAMP) indicates that the chelating phenolate groups contribute about 8 and 10 log units, respectively, to the stability constants.

On the basis of the equilibrium constants, the species distributions of 1:1 systems were calculated as a function of p[H], and selected results are illustrated in Figure 2. The maximum concentrations of the initial protonated mononuclear complexes occur at p[H] 2.9 for H_3LCu^{3+}, 6.4 for H_2LZn^{2+}, 7.7 for H_2LMn^{2+}, 5.7 for H_2LCd^{2+}, and 7.6 for H_3LCd^{3+}. It is important to observe that the Zn(II) and Mn(II) systems are composed primarily of mononuclear complexes, whereas dinuclear complexes are present in appreciable amounts in the 1:1 Cu(II) and Cd(II) systems, suggesting the latter metal ions have stronger tendencies to form dinuclear complexes with 24RBPyBC.

Homodinuclear Chelates of Divalent Ions. Titrations of the metal ions with H_6L^{4+} in 2:1 molar ratios were carried out to probe the homodinuclear complexes. The important characteristic for the 2:1 systems is that the dinuclear complexes are formed stepwise; i.e., the mononuclear species H_3LM^{3+} or H_2LM^{2+} are intermediates in the formation of the dinuclear complexes.

There are two inflections at *a* = 6 and *a* = 4 in the titration curves of the Zn(II) and Mn(II) systems (Figure 3). The inflection at *a* = 6 corresponds to the formation of the dinuclear complexes (whose maximum concentrations occur at p[H] 7.2 for Zn and 9.1 for Mn). The curves at *a* = 0−4 almost duplicate those of the corresponding 1:1 systems. As discussed above, the inflection at *a* = 4 corresponds to the formation of the mononuclear species MH_2L^{2+} where two phenolate are combined with the metal ion. Thus, addition of the second metal ion reacts so as to intercalate into the remaining sites of the macrocycle.

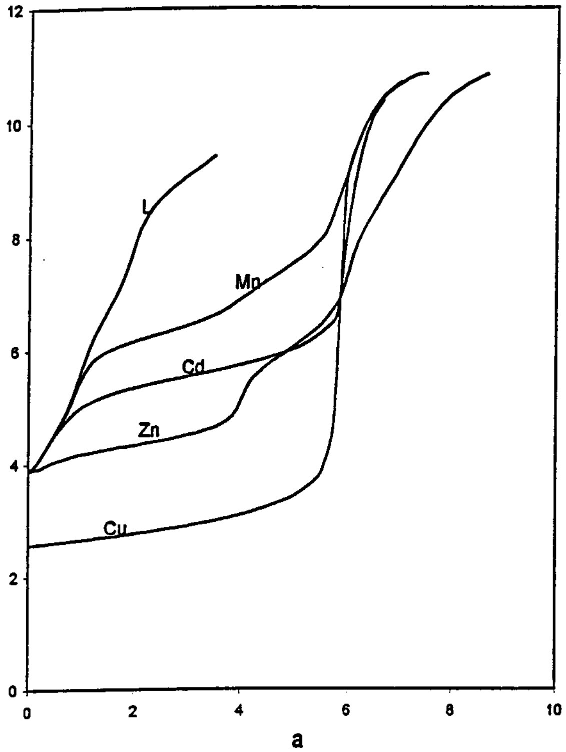


Figure 3. Potentiometric titration curves of the free ligand and 1:2 molar ratios of H_6L^{4+} with Cu(II), Cd(II), Mn(II), and Zn(II) at 25 °C, $\mu = 0.100$ M (KCl), where *a* is the moles of base added per mole of ligand present.

The titration curve for the Cu(II) system shows that the dinuclear species LCu_2^{2+} is formed at low p[H] values with a strong inflection at $a = 6$. Although there is no visually apparent inflection at $a = 3$, the species distribution diagram based on the stability constants reveals that, prior to the formation of the dinuclear species(LCu_2^{2+}), the major species formed is the mononuclear chelate H_3LCu^{3+}(90% at p[H] 2.4). The dinuclear complex where the second Cu(II) occupies the other half of the coordination sites of the macrocycle reaches its maximum concentration at p[H] 3.6.

The case for Cd(II) is relatively complicated. There is an inflection at $a = 6$ in the titration curve indicating the formation of LCd_2^{2+}. While there is no visual inflection at $a = 3$ or $a = 4$, the species distribution diagram (Figure 4) based on the stability constants illustrates that H_3LCd^{3+}(maximum of 27% at p[H] 5.5) and H_2LCd^{2+}(maximum of 24% at p[H] 5.8) are present together, before the dinuclear species reaches its maximum concentration at p[H] 7.9.

Another striking characteristic of 2:1 the systems is that hydrolysis of LM_2^{2+} occurs in alkaline solution in most cases to form hydroxo complexes. Monohydroxo $L(OH)M_2^{+}$ species are found in the Cd(II) and Mn(II) systems and are significant species above p[H] 10. However, the hydroxo species was not detected in the case of Cu(II), whereas both the monohydroxo and dihydroxo (or μ-oxo) species were observed for the Zn(II) system. It is important to note that the hydroxo species are not detected for the mononuclear complexes.

The overall and stepwise stability constants of dinuclear Cu(II), Cd(II), Zn(II), and Mn(II) complexes are listed in Table 1. Again, the dinuclear complex of Cu(II) is the most stable among the divalent metal complexes, with the decreasing stability order of Cu(II) >> Zn(II) > Cd(II) > Mn(II) for the overall stability constants β_{LM_2} ($2M^{2+} + L^{2-} \rightleftarrows LM_2^{2+}$).

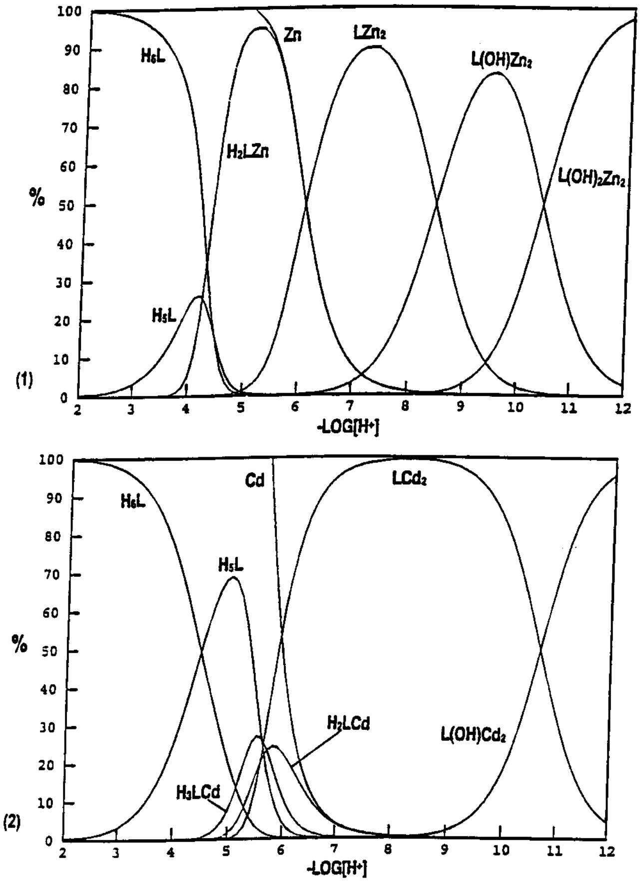


Figure 4. Species distribution diagrams indicating the species present as a function of p[H] in the systems containing 2:1 molar ratios of (1) Zn(II)−H_6L^{4+} and (2) Cd(II)−H_6L^{4+} at 25 °C, $\mu = 0.100$ M (KCl). % = percent of total concentration of ligand (1×10^{-3} M) set at 100%. The minor species (maximum content less than 5%) are omitted for clarity.

Heterodinuclear Chelates of Divalent Ions. On the basis of the coordination behavior of the mononuclear and homodinuclear complexes described above, the heterodinuclear complexes are expected to form with 24RBPyBC. Metal ions having the stronger affinity for the ligand will behave as leading metals in the formation of the heterodinuclear complexes. In this work, titrations of Cu−Cd, Zn−Cd, and Zn−Mn mixed metal complexes with H_6L^{4+} in 1:1:1 ratios were performed to investigate the behavior of the heterodinuclear complexes. The curves (Figure 5) present inflections at $a = 6$ for all mixed systems, as observed for the homodinuclear systems, indicating the formation of the heterodinuclear complexes LMM'^{2+}. Meanwhile, the curves for the Cu−Cd, Zn−Cd, and Zn−Mn systems present inflections at $a = 3$ or $a = 4$, corresponding respectively to the mononuclear species H_3LCu^{3+} or the mononuclear species H_2LZn^{2+}. This again confirms the fact that the dinuclear complexes are able to form stepwise. The stability constants of related heterodinuclear complexes are listed in Table 1. The magnitudes of the stability constants of the heterodinuclear complexes are found to be intermediate between those of the homodinuclear complexes involved. The heterodinuclear species (LMM'^{2+}) are formed with high yields in broad p[H] regions (6.8−10.2 for Zn−Cd, 7.0−10.3 for Cu−Cd, and 8.6−9.2 for Zn−Mn with 80% content; see also Figure 6). The monohydroxo species $LMM'(OH)^{+}$ are detected in all mixed systems, including the Cu−Cd case, as the content of LMM'^{2+} decreases.

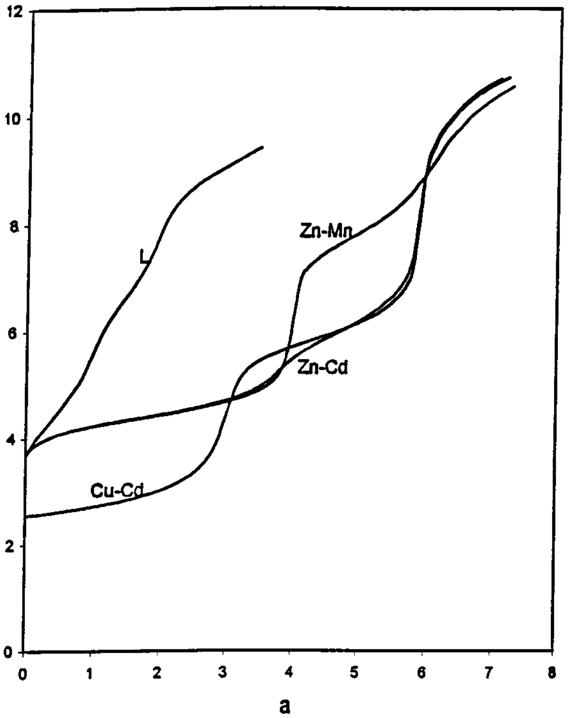


Figure 5. Potentiometric titration curves of the free ligand and its 1:1:1 molar ratio mixed systems with Cu(II)−Cd(II), Zn(II)−Cd(II), and Zn(II)−Mn(II) at 25 °C, $\mu = 0.100$ M (KCl), where *a* is the moles of base added per mole of the ligand present.

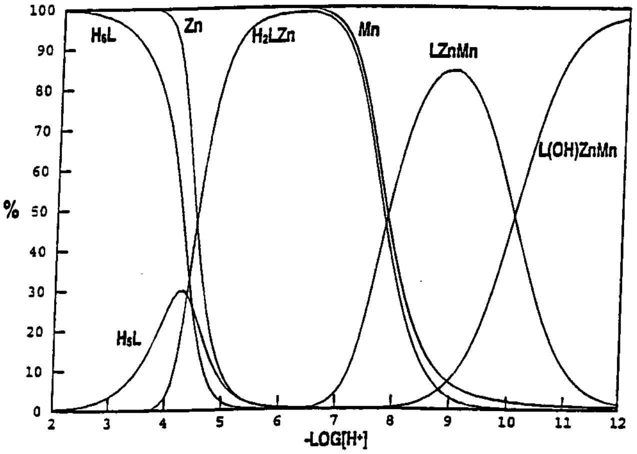


Figure 6. Species distribution diagram indicating the species present as a function of p[H] in the mixed system containing a 1:1:1 molar ratio of Zn(II)−Mn(II)−H_6L^{4+} at 25 °C, $\mu = 0.100$ M (KCl); % = percent of total concentration of the ligand (1×10^{-3} M) set at 100%. The minor species (maximum content less than 5%) are omitted for clarity.

The stability of the heterodinuclear complexes is also indicated by the following expected comproportionation equilibrium:

$$LM_2^{\ 2+} + LM'_2{}^{2+} \rightleftarrows 2LMM'^{\ 2+}$$

$$K_{com} = [LMM'^{\ 2+}]^2/[LM_2^{\ 2+}][LM'_2{}^{2+}]$$

The comproportionation constants are calculated from the constants of the homodinuclear and heterodinuclear complexes; log K_{com} = 3.20 for Zn−Cd, 2.08 for Zn−Mn, and 0.07 for Cu−Cd. The values of K_{com} indicate that the heterodinuclear complexes are more stable than the mixture of two homodinuclear complexes, particularly in the cases containing Zn. As discussed for the mononuclear chelates, Cu(II) and Cd(II) themselves have strong tendencies to form dinuclear complexes; thus, K_{com} for Cu−Cd is small but has a positive value.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for $[H_2LZn](NO_3)_2{\cdot}5H_2O$ and $[LZnCdCl_2]{\cdot}6H_2O$

	$[H_2LZn](NO_3)_2{\cdot}5H_2O$		
Zn(1)−O(1)	1.960(7)	Zn(1)−N(2)	2.050(8)
Zn(1)−O(2)	1.952(7)	Zn(1)−N(3)	2.201(8)
Zn(1)−N(1)	2.195(8)		
N(1)−Zn(1)−N(2)	78.4(3)	O(2)−Zn(1)−N(1)	108.7(3)
N(1)−Zn(1)−N(3)	154.1(3)	O(2)−Zn(1)−N(2)	123.7(3)
N(2)−Zn(1)−N(3)	78.31(3)	O(2)−Zn(1)−N(3)	93.3(3)
O(1)−Zn(1)−N(1)	92.7(3)	O(1)−Zn(1)−O(2)	102.8(3)
O(1)−Zn(1)−N(2)	133.2(3)	Zn(1)−O(2)−C(2)	118.8(6)
O(1)−Zn(1)−N(3)	95.6(3)	Zn(1)−O(1)−C(1)	118.7(6)
	$[LZnCdCl_2]{\cdot}6H_2O$		
Cd(1)−Cl(1)	2.603(3)	Zn(1)−O(1)	1.965(7)
Cd(1)−Cl(2)	2.572(4)	Zn(1)−O(2)	1.962(8)
Cd(1)−N(4)	2.409(9)	Zn(1)−N(1)	2.242(12)
Cd(1)−N(5)	2.341(9)	Zn(1)−N(2)	2.059(11)
Cd(1)−N(6)	2.409(9)	Zn(1)−N(3)	2.168(10)
Cd(1)−O(2)	2.414(8)		
N(4)−Cd(1)−N(5)	72.1(3)	N(1)−Zn(1)−N(2)	78.9(4)
N(4)−Cd(1)−N(6)	141.2(4)	N(1)−Zn(1)−N(3)	154.0(4)
N(5)−Cd(1)−N(6)	73.1(3)	N(2)−Zn(1)−N(3)	78.3(4)
N(4)−Cd(1)−O(2)	79.1(3)	O(1)−Zn(1)−N(1)	91.8(3)
N(5)−Cd(1)−O(2)	84.1(3)	O(1)−Zn(1)−N(2)	132.6(4)
N(6)−Cd(1)−O(2)	80.8(3)	O(1)−Zn(1)−N(3)	94.3(4)
N(4)−Cd(1)−Cl(1)	89.1(2)	O(2)−Zn(1)−N(1)	107.4(4)
N(5)−Cd(1)−Cl(1)	160.8(2)	O(2)−Zn(1)−N(2)	124.5(4)
N(6)−Cd(1)−Cl(1)	123.1(3)	O(2)−Zn(1)−N(3)	95.9(4)
N(4)−Cd(1)−Cl(2)	99.0(3)	O(1)−Zn(1)−O(2)	102.7(3)
N(5)−Cd(1)−Cl(2)	94.6(3)	Zn(1)−O(2)−Cd(1)	123.3(4)
N(6)−Cd(1)−Cl(2)	100.4(3)	Zn(1)−O(1)−C(1)	117.4(7)
O(2)−Cd(1)−Cl(1)	88.3(2)	Zn(1)−O(2)−C(17)	115.8(8)
O(2)−Cd(1)−Cl(2)	178.0(2)	Cd(1)−O(2)−C(17)	120.5(7)
Cl(1)−Cd(1)−Cl(2)	92.63(11)		

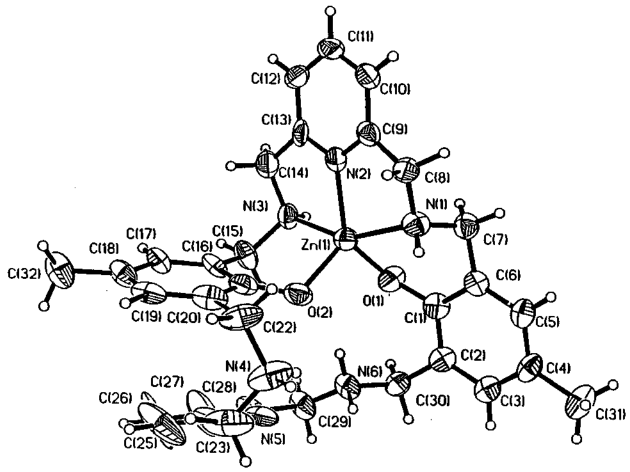


Figure 7. Structural diagram of $[H_2LZn](NO_3)_2{\cdot}5H_2O$ with the atom-labeling scheme.

Crystal Structure of $[H_2LZn](NO_3)_2{\cdot}5H_2O$. Crystals of $[H_2LZn](NO_3)_2{\cdot}5H_2O$ were obtained from a 1:1 Zn^{2+}:H_6L^{4+} aqueous solution at $a = 4$ with excess KNO_3. Selected bond lengths and angles are listed in Table 2, and the crystal structure is illustrated in Figure 7. The Zn(II) ion is coordinated with a distorted trigonal bipyramidal conformation by two phenolate groups and three nitrogen donors on one side of the macrocycle. Two phenolate oxygens and a pyridyl nitrogen form the basal plane, while two amino nitrogens occupy the axial sites. The three rings of the macrocycle associated with the Zn coordination

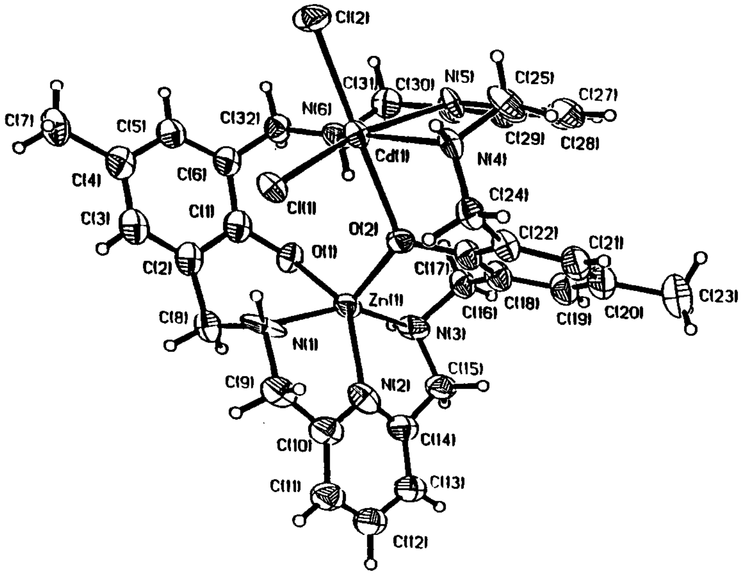


Figure 8. Structural diagram of $[LZnCdCl_2]\cdot 6H_2O$ with the atom-labeling scheme.

sphere (two phenyl rings and one pyridyl ring) are roughly perpendicular to the plane defined by Zn(1) O(1), O(2), and N(2).

The involvement of both phenolates is an unexpected development, since conventional wisdom might have predicted either penta- or hexacoordination of the zinc through the nitrogens, with the protonated phenols simply staying out of the way. This point would have been hard to prove spectrophotometrically also, since zinc is colorless. Yet the fact that the first and second protonation constants are so high, 12.3 and 11.5, respectively, would have pointed to the wrong conclusion. This structural finding will help researchers to rethink the microscopic structures of other phenolic/nitrogen ligands whose solution complex structures might have been incorrectly inferred on the basis of poteniometry alone. The fact that the H_2LZn complex forms substantially at pH ~5 (7 log units below pK^{H}_{1}) is remarkable indeed, and its low value is probably due to a combination of favorable chelate and macrocyclic effects.

Crystal Structure of $[LZnCdCl_2]\cdot 6H_2O$. Crystals of $[LZnCdCl_2]\cdot 6H_2O$ were obtained directly from the titration solution with KCl at $a = 6-7$ upon evaporation at room temperature. It is interesting to note that Zn has almost same coordination conformation, bond lengths, and bond angles as those in $[H_2LZn](NO_3)_2\cdot 5H_2O$. Only one oxygen atom of the phenolates bridges the Zn and Cd atoms (Figure 8).

The Cd(II) ion is hexacoordinated and is forced out of the plane formed by Zn(II), O(1), O(2), and N(2). The three nitrogen donors on one side of the macrocycle and one chloride form a basal plane, which is nearly perpendicular to the plane formed by Zn(II), O(1), O(2), and N(2). Another chloride and the bridging oxygen of the phenolate in the trans position complete the distorted octahedral coordination geometry. All bond distances and angles are normal.[17,18]

While the $ZnCdCl_2$ structure is interesting in its own right, it is somewhat disappointing that only one phenoxy group is bridged. The hexacoordination of Cd(II) is completed by the chloro ligands. This arrangement may be more favorable sterically than one involving both phenoxy groups as bridges. On the other hand, it may be possible that the weaker Cl^- ligand may be displaced in solution by the stronger phenoxy ligand, giving rise to a dibridged dinuclear complex in solution.

Both of these crystal structures are informative and provide strong support for the interpretation of the potentiometric results.

Experimental Section

Materials. The macrocyclic ligand was prepared from an HCl−MeOH solution by the method previously published.[11] All of the metal stock solutions for potentiometric studies were reagent grade chloride or bromide ($CdBr_2$) salt solutions prepared with doubly distilled water and standardized by EDTA. CO_2-free Dilute-it ampules of KOH were obtained from J. T. Baker Inc. KOH solutions (about 0.1 M) were prepared with doubly distilled water and standardized. The extent of carbonate accumulation ($\leq$1.8%) was checked periodically by titration with a standard HCl solution.

Potentiometric Equipment. A Corning 250 digital pH meter, fitted with Fisher full-range blue-glass and Fisher calomel reference electrodes, was used for potentiometric titrations. A Metrohm 10 mL capacity piston buret was used for precise delivery of the standard KOH. The solution to be studied was contained in a 75 mL jacketed glass cell thermostated at 25.00 ± 0.05 °C by a circulating constant-temperature water bath.

Potentiometric Determinations. All pH calibrations were performed with standardized HCl aqueous solutions to measure hydrogen ion concentrations directly ($p[H] = -\log [H^+]$). The ionic strength was adjusted to 0.100 M with KCl. Titrations of the ligand in the absence or presence of metal ions in aqueous solution were conducted in the manner described by Martell and Motekaitis.[19] Cell solutions (in general, 50.00 mL) were purged with a purified argon stream. Standard base was introduced into the sample solutions with a Metrohm piston buret. Experimental runs were carried out by adding increments of standard base to a solution containing H_6L^{4+} plus other components (KCl solution, metal solution). The concentrations of the sample solutions were 1×10^{-3} M for H_6L^{4+}. The titrations of free H_6L^{4+}, of $M-H_6L^{4+}$ in 1:1 and 2:1 ratios, and of $M-M'-H_6L^{4+}$ in a 1:1:1 ratio were carried out separately to investigate the mononuclear, homodinuclear, and heterodinuclear complexes. The p[H] range for accurate measurements was considered to be 2−12. The pK_w for the aqueous system, defined as $-\log([H^+][OH^-])$ at the ionic strength employed, was found to be 13.78.[19]

Computations. Protonation constants and stability constants from the direct titrations were calculated from the potentiometric data with the program BEST.[19] For the homometallic 1:1 and 2:1 systems, considering the possible dinuclear species existed in the 1:1 systems, values for the initial two sets of stability constants for the possible

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(19) Martell, A. E.; Motekaitis, R. J. *The Determination and Use of Stability Constants*, 2nd ed.; VCH Publishers: New York, 1992.

Table 3. Crystal Data and Structure Refinement Details for $[H_2LZn](NO_3)_2{\cdot}5H_2O$ and $[LZnCdCl_2]{\cdot}6H_2O$

	$[H_2LZn](NO_3)_2{\cdot}5H_2O$	$[LZnCdCl_2]{\cdot}6H_2O$
empirical formula	$C_{32}H_{48}N_6O_{13}Zn$	$C_{32}H_{48}Br_{0.05}CdCl_{1.95}N_6O_8Zn$
fw	818.15	894.65
cryst system	triclinic	monoclinic
space group	$P1$	$C2/c$
a, Å	10.7797(12)	16.234(5)
b, Å	10.9047(12)	15.976(9)
c, Å	17.0176(15)	29.829(11)
α, deg	106.857(9)	90
β, deg	95.822(8)	99.28(2)
γ, deg	100.191(9)	90
V, Å^3	1859.3(3)	7635(6)
Z	2	8
T, K	293(2)	293(2)
λ, Å	0.710 73	0.710 73
ρ(calcd), g/cm^3	1.461	1.557
abs coeff, mm^{-1}	0.735	1.429
R^a	0.1078	0.0972
$R_w{}^b$	0.1996	0.1522

[a] $R = \sum||F_o| - |F_c||/\sum F_o$. [b] $R_w = \{[\sum w(F_o{}^2 - F_c{}^2)^2]/[\sum w(F_o{}^2)^2]\}^{1/2}$.

mononuclear and dinuclear species were estimated. The mononuclear set of stability constants were first refined by the use of the 1:1 titration data with the second set fixed. Then the binuclear set were refined by the use of the 2:1 titration data with the mononuclear set fixed. The refinements were repeated until the differences between the calculated and observed p[H] values for both 1:1 and 2:1 systems were minimized. For the heterodinuclear system, with the stability constants of the mononuclear and homodinuclear species obtained above fixed, only the heterodinuclear set of constants were refined with the 1:1:1 titration data until the differences between the calculated and observed p[H] values were minimized. The error in the constants listed in Table 1 is estimated as ±0.04 log unit on the basis of the σ_{fit} value,[19] which measures the deviation of the experimental curve and the curve calculated from the equilibrium constants, being less than 0.01 p[H] unit in all potentiometric determinations. Species distribution diagrams were computed from the measured equilibrium constants with SPE and plotted with SPEPLOT.[19]

X-ray Structure Analyses. The crystals of $[H_2LZn](NO_3)_2{\cdot}5H_2O$ and $[LZnCdCl_2]{\cdot}6H_2O$ were each mounted on a glass fiber at room temperature. Preliminary examination and data collection were performed on a Siemens P4 diffractometer (Mo Kα radiation) at 293(2) K. Cell parameters were calculated from the least-squares fits of 25 high-angle reflections ($2\theta > 15°$). Data were collected with $5.0° \leq 2\theta \leq 50.0°$ at 293(2) K. For each complex, three standards, collected every 97 reflections, showed no significant trends. Lorentz and polarization corrections were applied to 6789 reflections for $[H_2LZn](NO_3)_2{\cdot}5H_2O$ and 6694 reflections for $[LZnCdCl_2]{\cdot}6H_2O$. Semiempirical absorption corrections were applied. A total of 6410 unique observed reflections for $[H_2LZn](NO_3)_2{\cdot}5H_2O$ ($R_{\mathrm{int}} = 0.0745$) and 6456 unique observed reflections for $[LZnCdCl_2]{\cdot}6H_2O$ ($R_{\mathrm{int}} = 0.1237$) were used in further calculations. The structures were solved by direct methods[20] and refined by full-matrix least-squares anisotropic refinements for all non-hydrogen atoms.[21] Crystal data and additional details regarding data collection and refinement are listed in Table 3.

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Supporting Information Available: Two X-ray crystallographic files in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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(20) Sheldrick, G. *SHELXS-86 Program for Crystal Structure Solution*; Institut für Anorganische Chemie, Universität Göttingen: Göttingen, Germany, 1986.

(21) Sheldrick, G. *SHELXL-97 Program for Crystal Structure Refinement*; Institut für Anorganische Chemie, Universität, Göttingen: Göttingen, Germany, 1997.