# Equilibria of Complex Formation Between Several Bivalent Metal Ions and Macrocyclic Tri- and Penta-amines

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Values of log $K_{ML}$, $\Delta H$, and $\Delta S$ (at $I$ 0.2 mol dm$^{-3}$ and 25 °C) have been determined potentiometrically or polarographically for the 1 : 1 reactions between $Zn^{II}$, $Cd^{II}$, $Hg^{II}$, or $Pb^{II}$ and macrocyclic polyamine ligands including 9- and 10-membered triamines and 15-, 16-, and 17-membered penta-amines. The resulting data are compared with those for the relevant linear polyamines. Whether in tri- or penta-amines, ligand cyclization has minor effects on the enthalpy change but has major effects on the entropy change on complex formation with these metal ions. The latter term is responsible for the increased stability of the macrocyclic complexes. This is opposite to the enthalpy-governed macrocyclic effect earlier reported for copper(II)–penta-amine complexes. Among the homologous macrocyclic ligands, the smallest ligands consistently show the highest affinity towards any of the metal ions tested, and this originates from the entropy term. A survey of the tri-, tetra-, and penta-amine systems indicates some correlation between large macrocyclic effects and the ratio of the size of the metal ion to the size of the macrocyclic cavity.

CYCLIZATION of linear polyamines affects the stabilities and selectivities of their complexes formed with metal ions.[1–17] Unusual stability and selectivity beyond mere cyclization effects sometimes occur when the ring size of a macrocyclic ligand and the size of the metal ion are matched. Such an interaction may be viewed as a host macrocyclic ligand to be recognized by a guest metal ion.[18] An example is the cyclization of the linear tetra-amine $L^8$ at the two terminal primary amine groups. Linkage by an ethylene group increases stability of the complex formed with $Cu^{II}$ by orders of 4—5,[6] whereas linkage by a propyl group results in increases of orders of 8—9.[7] Apparently, the latter 13-membered ($L^5$) ring cavity is more compatible with the ionic size of $Cu^{II}$ than is the former 12-membered ($L^4$) ring cavity.

Effects of cyclization and of macrocyclic ring size on complex stability are better understood by an analysis of the stability constant $K_{ML}$ in terms of the enthalpy $\Delta H$ and entropy $\Delta S$ of complex formation. These thermodynamic parameters are associated with metal, ligand, and/or complex structural features. We have now extended the previous studies on tetra-amine systems $L^4$—$L^8$ (refs. 6—9, 13,14) tri-($L^1$—$L^3$) and penta-amines $L^9$—$L^{12}$. The interaction of these polyamines with several bivalent metal ions including those of Cu, Zn, Cd, Hg, and Pb is described in this paper; the interaction with Cu has been partially presented.[13,15] Particular interests in the present study include: (*i*) whether $L^2$ forms a more stable complex than does $L^1$ with $Cu^{II}$, since we expect $L^2$ to suffer less steric rigidity at the *facial* configuration;[10,13,16] (*ii*) whether the host–guest relations hold between larger macrocycles and larger $Cd^{2+}$, $Hg^{2+}$, or $Pb^{2+}$ ions and between smaller macrocycles and smaller $Cu^{2+}$ or $Zn^{2+}$ ions; and (*iii*) the origin of macrocyclic effects in the tri- and penta-amine systems.

## EXPERIMENTAL

Macrocyclic triamines $L^1$ (as $L^1 \cdot 3HCl$) and $L^2$ (as $L^2 \cdot 3HBr$) were prepared by the method of Koyama and Yoshino.[19] The macrocyclic penta-amines $L^9$ (as $L^9 \cdot 5HCl$ or $\cdot 5HBr$), $L^{10}$ (as $L^{10} \cdot 5HBr$), and $L^{11}$ (as $L^{11} \cdot 5HBr$) were synthesized as described before.[15] The mixed protonation constants (log $K_1$ and $K_2$) determined by titration for $L^1$ are 10.80 and 7.09 (at 15 °C), 10.59 and 6.88 (25 °C), and 10.48 and 6.64 (35 °C). Those for $L^2$ are 11.15 and 6.95 (15 °C), 10.85 and 6.76 (25 °C), and 10.55 and 6.57 (35 °C). The log $K_i$ values for $L^9$—$L^{11}$ are listed in ref. 15 (presented as deprotonation constants). Values for the linear triamine $L^3$ and for the linear penta-amine $L^{12}$ were taken from the literature and corrected to $I = 0.2$ mol dm$^{-3}$.[20] Stock solutions of $Cu^{II}$, $Zn^{II}$, $Cd^{II}$ (all reagent grade sulphates, recrystallized once), and $Pb^{II}$ (as reagent grade nitrate) were

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[3] D. K. Cabbiness and D. W. Margerum, *J. Amer. Chem. Soc.*, 1970, **92**, 2151.

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[10] R. Yang and L. J. Zompa, *Inorg. Chem.*, 1976, **15**, 1499.

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[14] M. Kodama and E. Kimura, *J.C.S. Dalton*, 1977, 2269.

[15] M. Kodama and E. Kimura, *J.C.S. Dalton*, 1978, 104.

[16] L. Fabbrizzi and L. J. Zompa, *Inorg. Nuclear Chem. Letters*, 1977, **13**, 287.

[17] For a review see N. F. Curtis, *Co-ordination Chem. Rev.*, 1968, **3**, 3; D. H. Busch, K. Farmary, V. Goedken, V. Kotovic, A. C. Melnyk, C. R. Speranti, and N. Tokel, *Adv. Chem. Ser.*, 1971, **100**, 44; E. Kimura and M. Kodama, *Yuki Gosei Kagaku* (*J. Org. Synth. Chem.*), 1977, **35**, 632.

[18] D. J. Cram and J. M. Cram, *Science*, 1974, **183**, 803.

[19] H. Koyama and T. Yoshino, *Bull. Chem. Soc. Japan*, 1972, **45**, 481.

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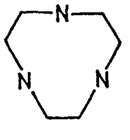
standardized by titration with ethylenediaminetetra-acetate (edta) using Eriochrome Black T.[21] All the other chemicals were reagent grade and were used without further purification.

*Potentiometric Titrations.*—Solutions (50 cm$^3$) of 1 : 11 ($c_L$ = 1.00 × 10$^{-3}$, $c_M$ = 11.0 × 10$^{-3}$ mol dm$^{-3}$), or 1 : 22 ($c_L$ = 0.50 × 10$^{-3}$, $c_M$ = 11.0 × 10$^{-3}$ mol dm$^{-3}$) $[H_5L]^{5+}$ (or $[H_3L]^{3+}$) : $M^{2+}$ ratio were titrated with carbonate-free aqueous solutions of 0.176 mol dm$^{-3}$ Na[OH]. Three titrations were conducted for each system; 3 min were required for equilibration of the Zn–L$^9$ and –L$^{10}$ systems, less for the other systems. The pH values were read with an Orion 701 digital pH meter. Values of −log[H$^+$] were estimated from the pH reading corrected for ionic-strength effects[22] (0.2 mol dm$^{-3}$) : −log[H$^+$] = pH −0.13. The electrode response was standardized with buffer solutions at pH 4.01 and 6.86 (25 °C). Humidified nitrogen gas free from carbon dioxide and oxygen was passed over the solution during the potentiometric measurements. Temperatures were controlled within ±0.05 °C by using a jacketed cell through which water from a constant-temperature bath was circulated.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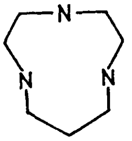
L$^1$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cyclodecane
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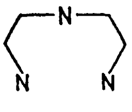
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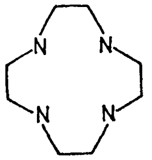
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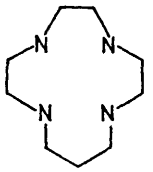
L$^4$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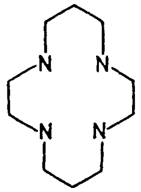
tridecane
L$^5$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tetradecane
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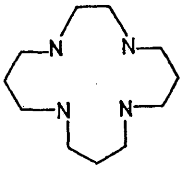
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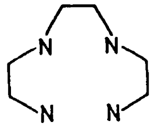
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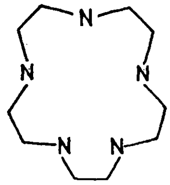
L$^8$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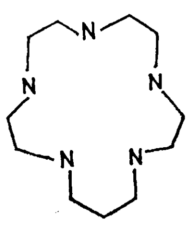
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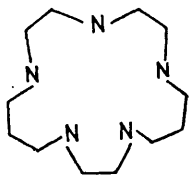
hexadecane
L$^{10}$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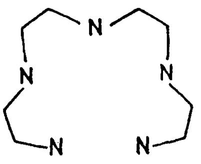
heptadecane
L$^{11}$


3,6,9-Triaza-
undecane-1,11-
diamine
L$^{12}$

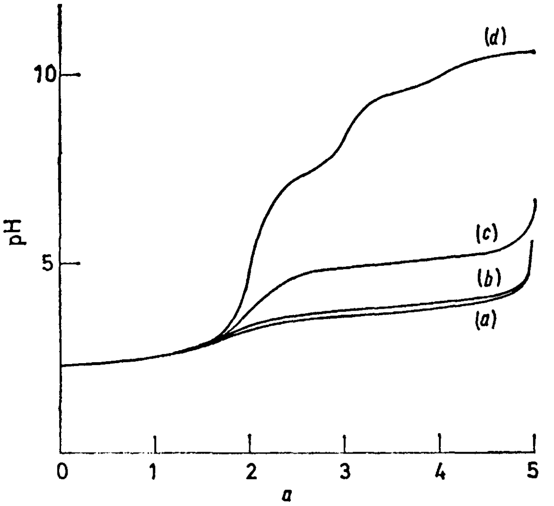


FIGURE 1 Titration curves of $[H_5L^{10}]^{5+}$ with [(*a*) Cd$^{II}$, (*b*) Zn$^{II}$, (*c*) Pb$^{II}$] and without [(*d*)] metal(II) ions at $c_L$ = 1.0 × 10$^{-3}$, $c_M$ = 11.0 × 10$^{-3}$, *I* 0.2 mol dm$^{-3}$, and 25 °C

The polarographic procedures (Method C) for Pb–L$^3$, Pb–L$^{12}$, and Cd–L$^3$ complexes were identical to those described earlier.[14,23] Stability constants for complexes of Hg$^{II}$ and L$^9$—L$^{12}$ were determined using the same polarographic apparatus as that for Hg and L$^4$—L$^8$ (Method A).[8] Another polarographic method (Method B) used for Zn–L$^1$ was identical to that for Zn$^{II}$ and L$^4$—L$^7$.[14] In all the measurements, ionic strength (*I*) was adjusted to 0.20 mol dm$^{-3}$ by adding an appropriate amount of sodium perchlorate. All the resulting thermodynamic quantities are shown in the Table, together with the relevant data previously reported, for comparison.

## RESULTS

*Potentiometric Determination of Stability Constants.*—*Complexes of* Zn$^{II}$, Cd$^{II}$, *and* Pb$^{II}$ *with the macrocyclic penta-amines* L$^9$—L$^{11}$. Typical titration curves are shown in Figure 1. It is obvious that Zn$^{2+}$, Cd$^{2+}$, and Pb$^{2+}$ ions interact with the macrocyclic penta-amines above *a* = 2, where *a* indicates the number of moles of base added per mol of ligand present. The titration curves in the buffer

$$M^{2+} + L \rightleftharpoons ML^{2+};\ K_{ML} = [ML^{2+}]/[M^{2+}][L] \quad (1)$$

$$[ML]^{2+} + H^+ \rightleftharpoons [M(HL)]^{3+};\quad K^H = [M(HL)^{3+}]/[ML^{2+}][H^+] \quad (2)$$

$$[H_{i-1}L]^{(i-1)+} + H^+ \rightleftharpoons [H_iL]^{i+};\quad K_i = [H_iL^{i+}]/[H_{i-1}L^{(i-1)+}][H^+] \quad (3)$$

region *a* = 2—5 were analyzed by assuming formation of a normal 1 : 1 complex $[ML]^{2+}$ and a monoprotonated complex $[M(HL)]^{3+}$, as found for Cu$^{II}$ and L$^9$—L$^{11}$.[15] The

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[21] G. Schwarzenbach and H. Flasckka, 'Die Kompl xometrische Titration,' Verlag Enke, Stuttgart, 1965.

[22] C. W. Davies, 'Ion Association,' Butterworths, Washington D.C., 1962.

[23] M. Kodama and E. Kimura, *Bull. Chem. Soc. Japan*, 1976, **49**, 2465.

complex formation and acid-base equilibria involved during titration are defined by equations (1)—(3). Based on this assumption, the total concentration of macrocycle, $c_L$, is expressed by (4) and (5). The sum of the hydrogen- and

$$c_L = [L]_F + [ML^{2+}] + [M(HL)^{3+}] \qquad (4)$$

where $[L]_F =$

$$[L] + [HL^+] + [H_2L^{2+}] + \ldots + [H_5L^{5+}] \qquad (5)$$

sodium-ion (from Na[OH]) concentrations, $\alpha$, at titration point $a$ is given by relation (6). By combining the above six equations one can derive relation (7). Here, $[M^{2+}]$ in equation (7) can be approximated by $c_M$. Contributions

$$\alpha = [H^+] + ac_L = 5[ML^{2+}] + 4[M(HL)^{3+}] + 5[L] + 4[HL^+] + 3[H_2L^{2+}] + 2[H_3L^{3+}] + [H_4L^{4+}] \qquad (6)$$

$$[\alpha(\alpha_H)_L - \beta_H c_L]/[M^{2+}] = K_{ML}\{(5c_L - \alpha) + K^H[H^+](4c_L - \alpha)\} \qquad (7)$$

where

$$(\alpha_H)_L = [L]_F/[L] = 1 + [H^+]K_1 + [H^+]^2K_1K_2 + \ldots + [H^+]^5K_1K_2K_3K_4K_5 \qquad (8)$$

and

$$\beta_H = 5 + 4[H^+]K_1 + 3[H^+]^2K_1K_2 + 2[H^+]^3K_1K_2K_3 + [H^+]^4K_1K_2K_3K_4 \qquad (9)$$

from hydrolyzed species such as $[M(OH)]^+$ have been neglected in view of the employed pH ($\leqslant 5.5$) and high p$K_a$ (hydrolysis constant) values for these metal ions.[20,24]

Thermodynamic quantities for metal–polyamine complexation [a]

| | | Ligand | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Triamine | | | Tetra-amine | | | | | Penta-amine | | | |
| $M^{2+}$ (ionic radius, $r$/Å) [b] | Thermodynamic quantity | $L^1$ | $L^2$ | $L^3$ | $L^4$ | $L^5$ | $L^6$ | $L^7$ | $L^8$ | $L^9$ | $L^{10}$ | $L^{11}$ | $L^{12}$ |
| $Cu^{2+}$ (0.72) | log $K_{ML}$ | 16.2 [c]<br>15.5 [j] | 14.4 [d] | 15.8 [e] | 24.8 [f] | 29.1 [g] | 27.2 [c] | 24.4 [h] | 20.2 [e] | 28.3 [i] | 27.1 [i] | 23.8 | 22.8 [i] |
| | $-\Delta H$/kcal mol$^{-1}$ | 13.0<br>14.2 [k] | 14.9 | 18.0 | 18.3 | 29.2 | 30.4<br>32.4 [l] | 26.5 | 21.6 | 32.9 | 32.7 | 27.2 | 25.0 |
| | $\Delta S$/cal K$^{-1}$ mol$^{-1}$ | 31<br>23.4 [k] | 16 | 12 | 51 | 34 | 22 | 23 | 19.5 | 22 | 14 | 18 | 21 |
| | log $K^H$ | | | | | | | | 5.5 | 4.3 | | 4.7 | 5.2 |
| $Zn^{2+}$ (0.74) | log $K_{ML}$ | 11.3 [d]<br>11.4 [n]<br>11.6 [j] | 10.3 [d] | 8.8 [e] | 16.2 [m] | 15.6 [m] | 15.5 [m]<br>15.0 [d] | 15.0 [m] | 12.1 [c] | 19.1 [d] | 17.9 [d] | 15.8 [d] | 15.1 [e] |
| | $-\Delta H$/kcal mol$^{-1}$ | 7.3<br>7.0 [n]<br>11.9 [k] | 6.7 | 6.5 | 7.9 | 7.8 | 7.6<br>7.9 [d]<br>14.8 [l] | 8.2 | 8.9 | 13.7 | 13.5 | 12.7 | 14.0 |
| | $\Delta S$/cal K$^{-1}$ mol$^{-1}$ | 27<br>29 [n]<br>13.2 [k] | 25 | 19 | 47 | 45 | 46<br>42 [d] | 41 | 25 | 41 | 37 | 30 | 23 |
| | log $K^H$ | | | | | | | | | 3.1 | 3.7 | 4.3 | |
| $Cd^{2+}$ (0.97) | log $K_{ML}$ | 9.2 [d] | 7.8 [d] | 8.2 [o] | 14.3 [m] | | | | 10.4 [e] | 19.2 [d] | 18.1 [d] | 15.5 [d] | 14.1 [e] |
| | $-\Delta H$/kcal mol$^{-1}$ | 7.6 | 7.3 | 10.1 | 8.2 | | | | 9.2 | 13.0 | 13.0 | 12.6 | 12.8 |
| | $\Delta S$/cal K$^{-1}$ mol$^{-1}$ | 17 | 11 | 4 | 38 | | | | 19 | 44 | 39 | 29 | 22 |
| | log $K^H$ | | | | | | | | | 3.4 | 3.9 | 4.2 | |
| $Hg^{2+}$ (1.10) | log $K_{ML}$ | | | | 25.5 [p] | 25.3 [p] | 23.0 [p] | 23.7 [p] | 24.5 [p] | 28.5 [q] | 27.4 [q] | 26.5 [q] | 24.8 [q] |
| | $-\Delta H$/kcal mol$^{-1}$ | | | | 23.6 | 24.7 | 32.9 | 24.7 | 30.2 | 32.7 | 34.4 | 33.4 | 33.4 |
| | $\Delta S$/cal K$^{-1}$ mol$^{-1}$ | | | | 38 | 34 | −4.9 | 26 | 11 | 20 | 10 | 9 | 1 |
| $Pb^{2+}$ (1.20) | log $K_{ML}$ | 10.8 [d] | 8.8 [d] | 7.4 [o] | 15.9 [m] | | | | 10.3 [m] | 17.3 [d] | 14.3 [d] | 11.6 [d] | 9.9 [o] |
| | $-\Delta H$/kcal mol$^{-1}$ | 8.2 | 7.3 | 8.5 | 6.6 | | | | 8.3 | 10.0 | 10.5 | 9.9 | 9.1 |
| | $\Delta S$/cal K$^{-1}$ mol$^{-1}$ | 27 | 16 | 5 | 51 | | | | 20 | 45 | 30 | 30 | 15 |
| | log $K^H$ | | | | | | | | | 3.8 | 5.0 | 5.3 | |

[a] The standard deviations for the present results are log $K_{ML} \pm 0.1$ (0.2), $\Delta H \pm 0.1$ (0.3), and $\Delta S \pm 1$ (2) for the pH-metric (polarographic) data. [b] D. L. Wright, J. H. Holloway, and C. N. Reilley, *Analyt. Chem.*, 1965, **37**, 884. [c] Ref. 13. [d] This work by the pH-metric method. At $I$ 0.2 mol dm$^{-3}$ and 25 °C. [e] See reference in footnote *b* and refs. therein. [f] Ref. 6. [g] Ref. 7. [h] Ref. 9. [i] Ref. 15. [j] Ref. 10. [k] Ref. 16. [l] Ref. 12. [m] Ref. 14. [n] This work by the polarographic method (Method B). At $I$ 0.2 mol dm$^{-3}$ and 25 °C. [o] This work by the polarographic method (Method C). At $I$ 0.2 mol dm$^{-3}$ and 25 °C. [p] Ref. 8. [q] This work by the polarographic method (Method A). At $I$ 0.2 mol dm$^{-3}$ and 25 °C.

Equation (7) may be rearranged to (10), and all the macrocyclic penta-amine systems afforded straight lines with

$$\frac{\alpha(\alpha_H)_L - \beta_H c_L}{[M^{2+}][H^+](4c_L - \alpha)} = K_{ML}\,\frac{(5c_L - \alpha)}{[H^+](4c_L - \alpha)} + K_{ML}K^H \qquad (10)$$

finite intercepts when $[\alpha(\alpha_H)_L - \beta_H c_L]/[M^{2+}][H^+](4c_L - \alpha)$ was plotted against $(5c_L - \alpha)/[H^+](4c_L - \alpha)$. Figure 2 presents data for the Zn–$L^{10}$ system. It can be concluded that under the present conditions $[ML]^{2+}$ and $[M(HL)]^{3+}$ are formed. The $K_{ML}$ values were determined from the gradient of the linear relation (10), and the $K^H$ values from the intercept/gradient. The $K_{ML}$ values were estimated at 15, 25, and 35 °C to obtain the thermodynamic parameters $\Delta H$ and $\Delta S$.

*Complexes of* Cu$^{II}$, Zn,$^{II}$ Cd$^{II}$, *and* Pb$^{II}$ *with the macrocyclic tri-amines* $L^1$ *and* $L^2$. All the systems showed inflections at $a = 1$ and 3. Assuming formation of only the $[ML]^{2+}$ species in the ensuing buffer region $a = 1$—3 (pH $\leqslant 6$), as was found for Cu– and Zn–$L^1$,[10] one obtains equation (11)

$$[\alpha(\alpha_H)_L - \beta_H c_L]/[M^{2+}] = K_{ML}(3c_L - \alpha) \qquad (11)$$

by applying the same treatment as above. The definitions for $\alpha$, $(\alpha_H)_L$, and $\beta_H$ are modified as follows:

$$c_L = [L]_F + [ML^{2+}] \qquad (12)$$

$$\alpha = [H^+] + ac_L = 3[ML^{2+}] + 3[L] + 2[HL^+] + [H_2L^{2+}] \qquad (13)$$

$$(\alpha_H)_L = 1 + [H^+]K_1 + [H^+]^2K_1K_2 + [H^+]^3K_1K_2K_3 \qquad (14)$$

$$\beta_H = 3 + 2[H^+]K_1 + [H^+]^2K_1K_2 \qquad (15)$$

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[24] F. Basolo and R. G. Pearson, 'Mechanisms of Inorganic Reactions,' 2nd edn., Wiley, New York, 1967, p. 31.

In all the systems, straight lines passing through the origin were obtained when $[\alpha(\alpha_H)_L - \beta_H c_L]/[M^{2+}]$ were plotted against $(3c_L - \alpha)$. A typical example for the Cd–L$^2$ system is shown in Figure 2. This is in agreement with the formation of $[ML]^{2+}$ as the only detectable complex species in the $a$ = 1—3 region of the titration curves. The $K_{ML}$ values were determined from the gradient of the linear relation (11). During titration of Pb–L$^2$ at 15 °C precipitation occurred a little before $a$ = 3, giving less accurate data. $\Delta H$ and $\Delta S$ were estimated from the temperature dependence of $K_{ML}$.

The present pH-metric procedure has been applied to the system Zn–L$^6$ to enable a comparison with the equilibrium quantities previously obtained polarographically (Method B).[14] The titration data are best analyzed by considering the formation of $[ML]^{2+}$ as the only complex species in the acidic region. The resulting equilibrium constants are in satisfactory agreement with the polarographic values (see Table).

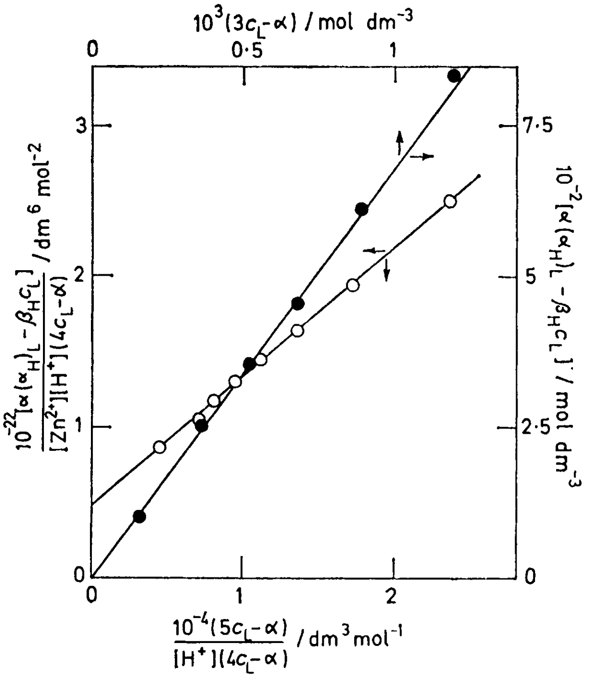

FIGURE 2 Plots for Zn$^{II}$–L$^{10}$ titration data according to equation (10) (○) and for Cd$^{II}$–L$^2$ data according to equation (11) (●) at $c_L = 1.0 \times 10^{-3}$, $c_M = 11.0 \times 10^{-3}$, $I$ 0.2 mol dm$^{-3}$, and 25 °C

*Polarographic Determination of Stability Constants.—Complexes of* Hg$^{II}$ *with macrocyclic* L$^9$—L$^{11}$ *and linear penta-amines* L$^{12}$ (*Method A*). The polarographic behaviours of the penta-amine solutions were the same as those of the tetra-amines.[8] Hence, $K_{HgL}$ was determined in an identical manner from the difference in $E_{\frac{1}{2}}$ of the anodic wave between edta (Y) and the penta-amines [using equation (4) of ref. 8]. The equilibrium constants of edta used for the calculation were log $K_1$ (for $Y^{4-} + H^+ \rightleftharpoons [HY]^{3-}$) 9.98, 9.80, and 9.60, log $K_2$ (for $[HY]^{3-} + H^+ \rightleftharpoons [H_2Y]^{2-}$) 6.25, 6.12, and 6.05, and log $K_{HgY}$ 22.5$_3$, 21.7$_6$, and 21.0$_4$, respectively, at 15, 25, and 35 °C.

*Complex of* Zn$^{II}$ *with the macrocyclic triamine* L$^1$ (*Method B*). Acetate buffer solutions contining Zn$^{II}$ and L$^1$ showed two reduction waves whose polarographic nature was the same as that found for the macrocyclic tetra-amine system.[14] The stability constant was determined accordingly as log $K_{ZnL}$ 11.4, in good agreement with the value of 11.3 or 11.6 determined potentiometrically by us or by Yang and Zompa.[10]

*Complexes of* Cd$^{II}$ *and* Pb$^{II}$ *with linear polyamines* (*Method C*). Stability constants for Pb–L$^3$, Pb–L$^{12}$, and Cd–L$^3$ were determined as for Pb–L$^8$.[14] Solutions containing large excesses of these ligands (pH > 8.6) gave well defined reversible two-electron reduction waves at the dropping mercury electrode (d.m.e.) which obey relations (2) and (3) of ref. 14. $\Delta H$ and $\Delta S$ were estimated from the temperature dependence of $K_{ML}$.

## DISCUSSION

The equilibrium constants for the Zn–L$^1$ complex determined by entirely independent experiments are in good agreement. Our values log $K_{ZnL}$ 11.3 (pH-metric) and 11.4 (polarographic) are nearly the same as the 11.6 (pH-metric, at $I$ 0.1 mol dm$^{-3}$) of Yang and Zompa.[10] Also, practically the same thermodynamic quantities were obtained for the Zn–L$^6$ system either polarographically (Method B) [14] or potentiometrically. These facts thus provide a good assessment of our procedures. It is puzzling, however, that for both the zinc complexes our $-\Delta H$ values are much smaller than those determined calorimetrically by other workers.[12,16] The reason for such wide discrepancies is not clear. We use our values for the following discussion. The log $K_{HgL}$ value of Hg–L$^{12}$ had been reported as 27.7 by Reilley and Holloway,[25] which is considerably larger than our value of 24.8. Our stability constant (log $K_{PbL}$ 9.9) for Pb–L$^{12}$ is within the reported range of 10—11.[25]

*Triamine System.—Copper*(II) *complexes.* The equilibrium of Cu–L$^1$ had been previously investigated by the polarographic method.[13] This technique, however, was not applicable to Cu–L$^2$ which gave irreversible waves. Hence, we turned to the pH-metric procedure.

It is most interesting that the complex formed by the ten-membered L$^2$ is no more stable than the nine-membered L$^1$, despite some improvement in the $\Delta H$ term. The anticipated release of the steric constraint by the ring expansion is thus reflected in $\Delta H$, but not in the total free-energy change due to the disadvantageous $\Delta S$ term. The assignment of the more favourable $\Delta H$ to stronger co-ordination bonds gets support from the shift to higher frequency (to 16 000 from 15 600 cm$^{-1}$ of Cu–L$^1$) [13] of the visible-absorption spectrum. The value of $\Delta H$ −14.9 kcal mol$^{-1}$ and ν(*d–d*) 16 000 cm$^{-1}$ are on the straight line previously established for copper(II)–polyamine (including L$^1$) complexes.[11,13,*] From a comparison of $\Delta H$ values for L$^2$ and linear L$^3$ it is evident that the release in steric strain is not enough to make up for the disadvantage suffered at the conversion from *meridional* to *facial* chelation accompanying cyclization of the triamine.[10]

*Zinc*(II) *complexes.* In contrast to the Cu system,

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[*] Throughout this paper: 1 cal = 4.184 J.

[25] C. N. Reilley and J. H. Holloway, *J. Amer. Chem. Soc.*, 1958, **80**, 2917.

cyclization of linear $L^3$ increases the complex stability. This arises mainly from the entropy term,* and may be explained in terms of the restricted conformational freedom of the cyclic ligands before chelation. Unlike the copper complexes, the $\Delta H$ term does not suffer an unfavourable effect, presumably because $Zn^{II}$ does not prefer a planar co-ordination geometry as does $Cu^{II}$. This also explains the fact that the $-\Delta H$ value for $L^3$ is not greater than for $L^1$ or $L^2$.

*Cadmium*(II) *complexes*. Cadmium(II) complexes of the macrocyclic ligands are less remarkably stabilized relative to those of zinc. The stabilization by the $\Delta S$ term is greatly offset by the unfavourable heat of reaction, suggesting an increase in steric strain. It is of interest that although Zn and Cd have a similar affinity for linear $L^3$, they differ appreciably in affinity for cyclic $L^1$ and $L^2$.

*Lead*(II) *complexes*. The complexes of $L^1$ and $L^2$ are more stable than that of $L^3$ due to the entropy contribution. Cyclization has little influence on the heat of complex formation.

*Penta-amine System.—Zinc*(II) *complexes*. Cyclization of linear $L^{12}$ results in $\Delta S$ terms which are quite favourable to complex formation and which are responsible for the increased stability of the macrocyclic $L^9$—$L^{11}$ systems. The $\Delta H$ terms are barely affected, suggesting little effect of steric strain on cyclization. The entropy-orientated macrocyclic effects for zinc(II)–penta-amine complexes are in contrast to the enthalpy-orientated effects of the copper(II) system.[15] At the moment we cannot pinpoint what causes this difference. Among the 15-, 16-, and 17-membered macrocycles, the smallest one forms the most stable complex with Zn or any other of the metal ions tested. This is without exception due to the entropy effect, indicating considerable configurational freedom remaining in the larger macrocycles.

Unlike the macrocyclic tri- or tetra-amine complexes, the macrocyclic penta-amine complexes are readily protonated at pH $< 6$. The extent of protonation tends to increase with increasing ring size.

*Cadmium*(II) *complexes*. The stability constant for the $L^9$ complex is five orders of magnitude larger than that for the $L^{12}$ complex. This is again due to entropy effects with no endothermic effect to counterbalance them. A comparison in reactivity between the Group 2B $Zn^{2+}$ and $Cd^{2+}$ ions indicates some size dependency: $Cd^{2+}$ forms less stable complexes than does Zn with tri- or tetra-amine macrocycles, while with the penta-amine macrocycles both cations form complexes having comparable stability constants. It is of interest that such a change at the penta-amines is caused by the $\Delta S$ values of the cadmium complexes becoming comparable to those for the zinc complexes. As for the $\Delta H$ values, the ring size results in little difference between the two Group 2B metal-ion complexes, which is not the case for another 2B metal, $Hg^{2+}$.

*Mercury*(II) *complexes*. Cyclization of $L^{12}$ enhances the affinity towards Hg by nearly four orders of magnitude, again by virtue of the entropy effect. The magnitude of this macrocyclic effect is remarkable in comparison with that for the tetra-amine system.[8] With tetra-amines, cyclization has a similar effect on the $\Delta S$ terms, but in a highly endothermic direction which scales down the otherwise large macrocyclic effects. Almost no endothermic effect in the present penta-amine case may indicate lack of steric strain within the penta-amine macrocyclic rings. In terms of thermodynamic quantities, the transition from macrocyclic tetra- to penta-amines in the mercury complexes is somewhat akin to the transition from macrocyclic tri- to tetra-amines in the copper complexes. Only small macrocyclic effects occur on going to the copper(II)–tri-amines and on going to the mercury(II)–tetra-amines due to the common thermodynamic causes. The large macrocyclic effects seen for the copper(II)–tetra-amine complexes share similar thermodynamic origins to those for the mercury(II)–penta-amines. The relative size of $Cu^{II}$ and $Hg^{II}$ might bring about such a distinction.

*Lead*(II) *complexes*. The Pb–$L^9$ complex is more than seven orders of magnitude more stable than Pb–$L^{12}$, mostly due to the $\Delta S$ effect. This order of enhancement in stability is significantly higher than those for the tri-amine (3—4 orders) or tetra-amine systems (5—6 orders), which may be another manifestation of some correlation between the size of the metal ions and size of the macrocyclic cavities.

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* Citing their experimental data, Fabbrizzi and Zompa advocated the enthalpy effect.[16]