Equilibria and Kinetics of Complex Formation Between Zinc(II), Lead(II), and Cadmium(II), and 12-, 13-, 14-, and 15-Membered Macrocyclic Tetra-amines

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Polarographic methods have been used to determine the equilibria and kinetics of reaction of Zn^{II}, Pb^{II}, and Cd^{II} with 12- to 15-membered macrocyclic tetra-amines including 1,4,7,10-tetra-azacyclododecane (L^1), 1,4,7,10-tetra-azacyclotridecane (L^2), 1,4,8,11-tetra-azacyclotetradecane (L^3), and 1,4,8,12-tetra-azacyclopentadecane (L^4) in acetate buffer solutions. Unlike the copper(II) system, the stability constants of the zinc complexes hardly change with macrocyclic ring size: $\log K_{ZnL}$ = 16.2, 15.6, 15.5, and 15.0 for L^1, L^2, L^3, and L^4, respectively (I 0.20 mol dm^{-3} and 25°C). The much larger Cd^{II} and Pb^{II} form complexes only with L^1: $\log K_{CdL}$ 14.3 and $\log K_{PbL}$ 15.9. The 10^3—10^5 times greater stabilities of the macrocyclic complexes compared with the related complexes of linear tetra-amines are all due to favourable entropy changes, regardless of the metal-ion size. The rate law for complex formation in acetate buffers is $d[ML]/dt = k_H[M(O_2CMe)^+][HL^+] + k_{2H}[M(O_2CMe)^+][H_2L^{2+}]$ for all the metal ions. A comparison with reactions of Cu^{II} and L^1—L^4 shows that the values of k_H parallel the well established rates of water exchange of the aquametal ions.

As part of our continuing investigation [1-6] of the macrocyclic effect,[7-9] we have now studied the thermodynamics and kinetics of complex formation of Zn^{II}, Cd^{II}, and Pb^{II} with tetra-amine macrocycles having 12- to 15-membered rings, including 1,4,7,10-tetra-azacyclododecane (L^1), 1,4,7,10-tetra-azacyclotridecane (L^2), 1,4,8,11-tetra-azacyclotetradecane (L^3), and 1,4,8,12-tetra-azacyclopentadecane (L^4). Polarograms of the fully equilibrated metal(II) macrocycle systems in acetate

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[1] M. Kodama and E. Kimura, *J.C.S. Chem. Comm.*, 1975, 326.

[2] M. Kodama and E. Kimura, *J.C.S. Dalton*, 1976, 116.

[3] M. Kodama and E. Kimura, *J.C.S. Chem. Comm.*, 1975, 891.

[4] M. Kodama and E. Kimura, *J.C.S. Dalton*, 1976, 1720.

[5] M. Kodama and E. Kimura, *J.C.S. Dalton*, 1976, 2341.

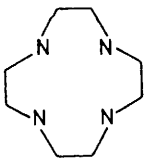
[6] M. Kodama and E. Kimura, *J.C.S. Dalton*, 1976, 2335.

[7] D. K. Cabbiness and D. W. Margerum, *J. Amer. Chem. Soc.*, 1969, **91**, 6540.

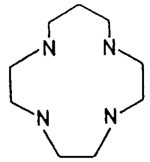
[8] D. K. Cabbiness and D. W. Margerum, *J. Amer. Chem. Soc.*, 1970, **92**, 2151.

[9] For a review, see J. J. Christensen, D. J. Eatough, and R. M. Izatt, *Chem. Rev.*, 1974, **74**, 351; D. H. Busch, K. Farmery, V. Goedken, V. Katovic, A. C. Melnyk, C. R. Sperati, and N. Tokel, *Adv. Chem. Ser.*, 1971, **100**, 52; L. F. Lindy, *Chem. Soc. Rev.*, 1975, 421.

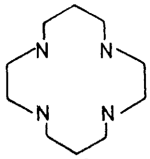
buffers invariably display two diffusion-controlled reduction waves, one assignable to free metal ions and the other to metal ion bound to the macrocycle. The stability constants of the macrocyclic complexes could thus be determined by comparing the wave-height for the free M^{2+} with that for the total M^{2+}. With Cd^{II} and Pb^{II}, stable complexes are only formed with the relatively small macrocycle L^1. We have also determined equilibrium functions for the reactions of Pb^{II} with 3,6-diazoctane-1,8-diamine (L^5) and 3,7-diazanonane-1,9-diamine (L^6) to serve as references for the macrocyclic systems. The kinetic rates of complex formation were determined, as before,[1-5] by following the decrease in the wave-heights of the uncomplexed metal ions.



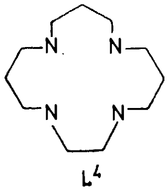
L^1



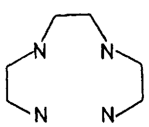
L^2



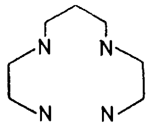
L^3



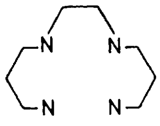
L^4



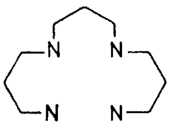
L^5



L^6



L^7



L^8

EXPERIMENTAL

The macrocyclic ligands, L^1 (prepared by the method of Stetter and Mayer [10] and Collman and Schneider [11]) and L^2, L^3, and L^4 (prepared by the method of Martin *et al.*[12]), were purified by twice recrystallizing from 6N HCl.[2,4,5] Solutions of zinc(II) nitrate and cadmium(II) nitrate were prepared by dissolving a known amount of the metals (99.999% pure) in dilute nitric acid and by removing the excess of HNO_3 by distillation under reduced pressure. A standard solution of lead(II) nitrate was prepared by dissolving a known amount of crystals of pure $Pb[NO_3]_2$ in redistilled water. Commercially available L^5 was purified by the method of Jonassen and Strickland [13] and L^6 (Eastman) was purified as described by Hinz and Margerum.[14] All the other chemicals were of analytical reagent grade and were used without further purification. The polarographic apparatus and kinetic procedures were identical to those described previously.[2,4]

RESULTS

Equilibrium Studies.—In the presence of the macrocyclic ligands, in acetate-buffered solutions, the metal ions displayed two diffusion-controlled polarographic waves at a dropping mercury electrode (d.m.e.) after equilibration for 2 h (Zn) or 30 min (Cd and Pb). An example for the Zn^{II}–L^2 system is shown in Figure 1. The first waves consistently appeared at the reduction potentials of the free metal ion, and the second ones at more negative potentials. Assuming that the first wave corresponds to reduction of the equilibrated hydrated acetatometal(II) ion and the second wave to reduction of the macrocyclic complex ions, then relation (1) defining the complex stability constant, K_{ML}, should be obeyed. Here: $(\alpha_H)_L =$

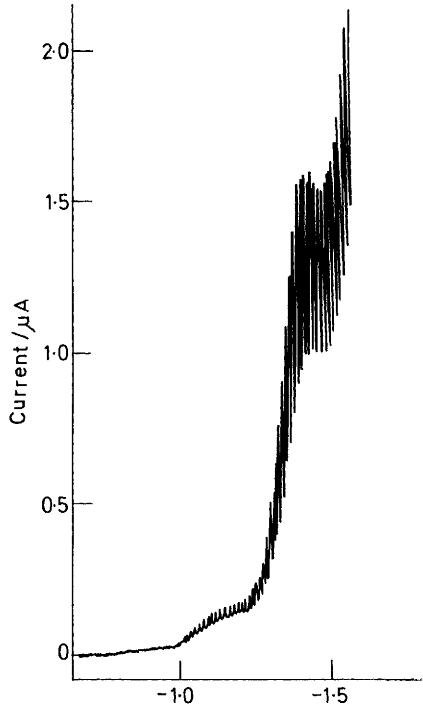


FIGURE 1 Polarogram of a solution containing Zn^{2+} (0.288×10^{-3} mol dm^{-3}), L^2 (0.385×10^{-3} mol dm^{-3}), and $[MeCO_2^-]$ (0.10 mol dm^{-3}) at pH 5.50, I 0.20 mol dm^{-3}, and 15.0 °C

$$\frac{K_{ML}}{(\alpha_H)_L\beta_{MeCO_2}} = \frac{[ML^{2+}]}{[M^{2+}]_f[L]_f} = \frac{(i_0 - i_1)}{i_1} \cdot \frac{i_0}{c_M}\left[\left(\frac{c_L}{c_M} - 1\right)i_0 + i_1\right]^{-1} \quad (1)$$

$[L]_f/[L] \approx [H^+]^2/K_1{}^Hk_2{}^H$ in the pH region under study ($K_i{}^H$ is the deprotonation constant for $H_iL^{i+} \rightleftharpoons H_{i-1}L^{(i-1)+} + H^+$);[2,4,5] i_0 is the reduction wave-height

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[10] H. Stetter and K. H. Mayer, *Chem. Ber.*, 1961, **94**, 1410.

[11] J. P. Collman and P. W. Schneider, *Inorg. Chem.*, 1966, **5**, 1380.

[12] L. Y. Martin, L. J. DeHayes, L. J. Zompa, and D. H. Busch, *J. Amer. Chem. Soc.*, 1974, **96**, 4046.

[13] H. B. Jonassen and G. T. Strickland, *J. Amer. Chem. Soc.*, 1958, **80**, 312.

[14] F. P. Hinz and D. W. Margerum, *Inorg. Chem.*, 1974, **13**, 2941.

TABLE 1

Equilibrium data for reactions of macrocyclic tetra-amines with metal(II) ions at 25 °C and $I = 0.20$ mol dm^{-3} [see equation (1)]

$10^3 c_M$ [a]	$10^3 c_L$ [a]	pH	$[MeCO_2^-]$ [a]	$10^{-3} K'$ [b]	$10^{-15} K'(\alpha_H)_L$	$10^{-4} K'\beta_{MeCO_2}$
				dm^3 mol^{-1}		
Zn^{II}–L^1						
0.20	0.40	4.02	0.10	4.6	11	
	0.40	4.10	0.10	7.0	11	
	0.40	4.20	0.10	11	11	1.6
	0.40	4.41	0.10	28	11	
	0.40	4.75	0.10	140	11	
	0.40	4.98	0.10	390	11	
	0.40	4.20	0.025	14		1.6
	0.40	4.20	0.050	13		1.6
	0.40	4.20	0.20	8.3		1.6
	0.30	4.10	0.10	7.1		
	0.60	4.10	0.10	6.9		
	0.80	4.10	0.10	6.9		
	1.20	4.10	0.10	6.9		
	1.60	4.10	0.10	7.0		
Zn^{II}–L^2						
0.20	0.40	4.30	0.05	0.52	2.1	
	0.40	4.82	0.05	5.6	2.0	0.68
	0.40	5.22	0.05	34	2.0	
	0.40	4.82	0.10	4.7		0.68
	0.40	4.82	0.20	3.6		0.68
	0.60	4.82	0.05	5.6		
	0.80	4.82	0.05	5.6		
	1.20	4.82	0.05	5.6		
	1.60	4.82	0.05	5.5		
Zn^{II}–L^3						
0.20	0.40	4.90	0.10	2.2	2.2	
	0.40	5.01	0.10	3.5	2.1	
	0.40	5.23	0.10	10	2.2	1.5
	0.40	5.45	0.10	27	2.2	
	0.40	5.85	0.10	140	2.2	
	0.40	5.23	0.025	13		1.4
	0.40	5.23	0.050	12		1.5
	0.40	5.23	0.20	7.8		1.5
	0.30	5.23	0.10	10		
	0.60	5.23	0.10	10		
	0.80	5.23	0.10	10		
	1.20	5.23	0.10	10		
Zn^{II}–L^4						
0.10	0.20	5.30	0.20	11	0.52	
	0.20	5.50	0.20	26	0.52	
	0.20	5.66	0.20	55	0.53	
	0.20	5.81	0.20	110	0.53	
	0.20	5.35	0.20	11		0.21
	0.20	5.35	0.10	15		0.21
	0.20	5.35	0.05	18		0.21
	0.40	5.35	0.20	11		
	0.60	5.35	0.20	11		
	1.00	5.35	0.20	10		
Pb^{II}–L^1 (at 27 °C)						
0.286	0.547	4.70	0.10	3.8	0.38	
	0.547	5.10	0.10	22	0.36	40
	0.547	5.48	0.10	120	0.32	
	0.386	5.10	0.10	25		
	0.800	5.10	0.10	24		
	1.930	5.10	0.10	21		
	0.547	5.10	0.05	47		39
	0.547	5.10	0.20	9.3		40
Cd^{II}–L^1						
0.100	0.234	5.20	0.10	7.6	0.083	2.0
	0.234	5.51	0.10	34	0.081	
	0.234	5.80	0.10	150	0.083	
	0.468	5.20	0.10	7.6		
	0.702	5.20	0.10	7.6		
0.200	0.468	5.20	0.10	7.6		
0.300	0.468	5.20	0.10	7.6		
0.100	0.234	5.20	0.05	11		2.0
	0.234	5.20	0.20	4.9		2.0

[a] Units mol dm^{-3}. [b] The right-hand side of equation (1).

of M^{2+} in the absence of macrocycles and i_1 the wave-height of the first wave; $\beta_{MeCO_2} = [M^{2+}]_f/[M^{2+}(aq)] = 1 + K_{M(O_2CMe)}[MeCO_2^-] + K_{M(O_2CMe)}K_{M(O_2CMe)_2}[MeCO_2^-]^2$ and $[M^{2+}]_f = [M^{2+}(aq)] + [M(O_2CMe)^+] + [M(O_2CMe)_2]$; for M = Zn and Cd the term involving $M[O_2CMe]_2$ is omitted * (for the values of $K_{M(O_2CMe)}$ and $K_{M(O_2CMe)_2}$ at various temperatures see ref. 15); $[L]_f$ is the concentration of uncomplexed macrocycle; and c_M and c_L are respectively the initial concentrations of M^{2+} and macrocycle. Equation (1) was derived by use of $[ML^{2+}] = [(i_0 - i_1)/i_0]c_M$, $[M^{2+}]_f = (i_1/i_0)c_M$, and $[L]_f = \{(c_1c_M) - [(i_0 - i_1)/i_0]\}c_M$.

The results were, as predicted from equation (1), that the right-hand side multiplied by $(\alpha_H)_L$ or β_{MeCO_2} was constant when $[MeCO_2^-]$ or $[H^+]$ were kept constant, and that the right-hand side was independent of c_L and c_M when $[MeCO_2^-]$ and $[H^+]$ were kept constant. Typical results are shown in Table 1. The stability constants were estimated with the aid of equation (1) at several temperatures in order to assess thermodynamic parameters for the complex formation (Figure 2). All the equilibrium results are listed in Table 2.† The mixed deprotonation constants obtained experimentally at these temperatures were used to calculate $(\alpha_H)_L$ (Table 3). Values of K_i^H, $K_{M(O_2CMe)}$, and $K_{M(O_2CMe)_2}$ at temperatures other than those listed were estimated by interpolation.

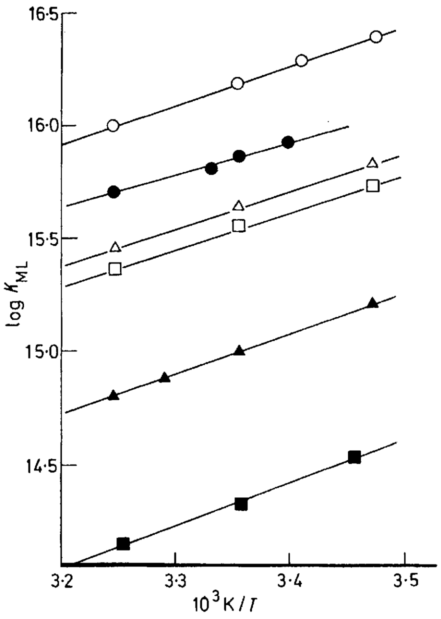

FIGURE 2 van't Hoff plots of stability constants for the complexes $[ZnL^1]^{2+}$ (○), $[PbL^1]^{2+}$ (●), $[ZnL^2]^{2+}$ (△), $[ZnL^3]^{2+}$ (□), $[ZnL^4]^{2+}$ (▲), and $[CdL^1]^{2+}$ (■)

The systems Pb^{II}–L^5 *and* Pb^{II}–L^6. Lead(II) ions in solutions containing large excesses of L^5 or L^6 ($8.3 < pH < 9.5$) gave a well defined cathodic wave at the d.m.e. with its limiting current proportional to the total $[Pb^{2+}]$ and to the square root of the effective mercury pressure. Plots of log $[i/(i_d - i)]$ against d.c. potential, E, gave straight lines having reciprocal gradients of −32 mV for L^5 and −34 mV for L^6, representing a reversible two-electron reduction for both systems. The half-wave potentials of the lead(II) complexes, $(E_{\frac{1}{2}})_{PbL}$, shifted according to relations (2) and (3) (see Table 4), where $[L]_f$ is the concentration of

$$\Delta(E_{\frac{1}{2}})_{PbL}/\Delta\log[L]_f = -30 \text{ mV} \qquad (2)$$

$$\Delta(E_{\frac{1}{2}})_{PbL}/\Delta\log(\alpha_H)_L = 30 \text{ mV} \qquad (3)$$

free ligand and $(\alpha_H)_L = 1 + ([H^+]/K_1^H) + ([H^+]^2/K_1^HK_2^H)$ in the present pH region.[17] Thus, the formation constants of the 1 : 1 lead(II) complexes, K_{PbL}, were determined from equation (4) (see ref. 2 and references therein), where

TABLE 2

Comparison of stability constants, and enthalpies and entropies of tetra-amine complex formation, at 25 °C [a]

Complex	log (K_{ML}/dm³ mol⁻¹)	−ΔH / kcal mol⁻¹	ΔS / cal K⁻¹ mol⁻¹	I / mol dm⁻³
$[ZnL^1]^{2+}$	16.2 ± 0.2	7.9 ± 0.4	47 ± 2	0.2
$[ZnL^2]^{2+}$	15.6 ± 0.2	7.8 ± 0.4	45 ± 2	0.2
$[ZnL^3]^{2+}$	15.5 ± 0.2	7.6 ± 0.4	46 ± 2	0.2
$[ZnL^4]^{2+}$	15.0 ± 0.5	8.2 ± 0.5	41 ± 4	0.2
$[ZnL^5]^{2+}$ [b]	12.1	8.9	25.0	0.1
$[ZnL^6]^{2+}$ [b]	12.8	11.9	18.8	0.5
$[ZnL^7]^{2+}$ [b]	11.3	10.6	15.9	0.5
$[ZnL^8]^{2+}$ [b]	9.3	7.4	18.0	0.1
$[CuL^1]^{2+}$ [c]	24.8	18.3	51.4	0.2
$[CuL^2]^{2+}$ [d]	29.1	29.2	33.7	0.2
$[CuL^4]^{2+}$ [e]	24.4	26.5	22.7	0.2
$[CuL^5]^{2+}$ [b]	20.2	21.6	19.5	0.1
$[CuL^6]^{2+}$ [b]	23.9	27.7	16.5	0.5
$[CuL^7]^{2+}$ [b]	21.8	25.9	13.1	0.5
$[CuL^8]^{2+}$ [b]	17.3	19.5	12.8	0.1
$[NiL^3]^{2+}$ [f]	22.2	31.0	−2	0.1
$[NiL^6]^{2+}$ [f]	15.8	19.4	7.2	0.1
$[CdL^1]^{2+}$	14.3 ± 0.2	8.2 ± 0.5	38 ± 2	0.2
$[CdL^5]^{2+}$ [g]	10.4	9.2	19	0.1
$[PbL^1]^{2+}$	15.9 ± 0.2	6.6 ± 0.5	51 ± 2	0.2
$[PbL^5]^{2+}$	10.3 ± 0.3	8.3 ± 0.5	20 ± 1	0.2
$[PbL^6]^{2+}$	7.8 ± 0.3	7.3 ± 0.5	11 ± 1	0.2
$[HgL^1]^{2+}$ [h]	25.5	23.6	38	0.2
$[HgL^5]^{2+}$ [h]	24.5	30.2	11	0.2

[a] Uncertainties are the standard deviations. [b] Ref. 19. [c] Refs. 1 and 2. [d] Refs. 3 and 4. [e] Ref. 5. [f] Refs. 14 and 21. [g] Ref. 18 and D. L. Wright, J. H. Holloway, and C. N. Reilley, *Analyt. Chem.*, 1965, **47**, 2011. [h] Ref. 6.

TABLE 3

First and second mixed deprotonation constants (pK_1^H and pK_2^H) of macrocyclic tetra-amines at I = 0.20 mol dm⁻³ (Na[ClO₄])

Ligand	pK_i^H value at 35	25	15 °C
L_1, pK_1^H	10.5_1	10.7_0	10.9_1
pK_2^H	9.4_9	9.7_0	9.9_0
L^2, pK_1^H	10.9_0	11.1_0	11.3_0
pK_2^H	9.9_1	10.1_0	10.3_1
L^3, pK_1^H	11.2_3	11.5_0	11.8_2
pK_2^H	10.1_5	10.3_0	10.5_0
L^4, pK_1^H	11.0_0	11.2_0	11.4_0
pK_2^H	9.9_0	10.1_0	10.3_0

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* Since $Zn[O_2CMe]_2$ and $Cd[O_2CMe]_2$ species were not detected in solutions [15] under the same conditions as ours, we have ignored their participation in the present system.

† A further guide to the reliability of the derived data is obtained from the stability constant (log K_{ZnL} 11.4 at I 0.2 mol dm⁻³ and 25 °C) of the zinc(II)-1,4,7-triazacyclononane complex, which was determined by use of the same polarographic method (unpublished results) and which is in good agreement with the value (11.6) determined by Yang and Zompa using a titration method.[16]

[15] N. Tanaka and K. Kato, *Bull. Chem. Soc. Japan*, 1960, **33**, 417, 1412.

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

[17] The literature values are corrected to I = 0.2 mol dm⁻³; D. C. Weatherburn, E. J. Billo, J. P. Jones, and D. W. Margerum, *Inorg. Chem.*, 1970, **9**, 1557; R. Barbucci, L. Fabbrizzi, and P. Paoletti, *J.C.S. Dalton*, 1972, 745.

d = diffusion-current constant and $\log(d_{PbL}/d_{Pb})$ was experimentally determined at $[PbX] = [Pb^{2+}]$ to be 0.067 for L^5

$$\Delta(E_{\frac{1}{2}}) = (E_{\frac{1}{2}})_{Pb} - (E_{\frac{1}{2}})_{PbL} = 0.0296\left\{\log\frac{K_{PbL}[L]_f}{(\alpha_H)_L} + \log\frac{d_{PbL}}{d_{Pb^{2+}}}\right\} \quad (4)$$

and 0.065 for L^6. Values of $\log K_{PbL}$ of 10.48, 10.31, and 10.10 at 16.0, 25.0, and 34.0 °C, respectively, gave ΔH −8.3 ± 0.5 kcal mol^{-1} and ΔS 20 ± 1 cal K^{-1} mol^{-1} (at I 0.2 mol dm^{-3}) for L^5.* Our value of $\log K$ is in good agreement with the value of 10.4 reported by Reilley and Schmid.[18] Values of $\log K_{PbL}$ of 7.97, 7.82, and 7.63 at 15, 25, and 34 °C, respectively, gave ΔH −7.3 ± 0.5 kcal mol^{-1} and ΔS 11 ± 1 cal K^{-1} mol^{-1} for L^6. These data are included in Table 2.

TABLE 4

Effects of ligand concentration and pH on the half-wave potentials of complexes Pb–L^5 and Pb–L^6 at $[Pb^{2+}]$ = 2.5 × 10^{-4} mol dm^{-3}, I = 0.20 mol dm^{-3}, and 25 °C

$10^3[L]_f$ / mol dm^{-3}	pH	$(\alpha_H)_L$	$(E_{\frac{1}{2}})_{PbL}$ / V *versus* s.c.e.	$\Delta(E_{\frac{1}{2}})_{PbL}$/mV calc.	$\Delta(E_{\frac{1}{2}})_{PbL}$/mV obs.
L^5					
150	9.38	8.48	−0.638	0 [a]	0
100	9.38	8.48	−0.634	5.3 [a]	4
50	9.38	8.48	−0.624	14.3 [a]	14
100	9.38	8.48	−0.634	0 [b]	9
100	8.80	64.8	−0.609	26.4 [b]	25
100	8.34	445	−0.584	50.9 [b]	50
L^6					
12	9.50	13.5	−0.524	0 [a]	0
20	9.50	13.5	−0.531	−6.6 [a]	−7
40	9.50	13.5	−0.538	−15.7 [a]	−14
70	9.50	13.5	−0.549	−22.7 [a]	−25
20	8.35	620	−0.478	0 [b]	0
20	8.80	154	−0.496	−17.9 [b]	−18
20	9.50	13.5	−0.531	−49.4 [b]	−53

[a] Using equation (2). [b] Using equation (3).

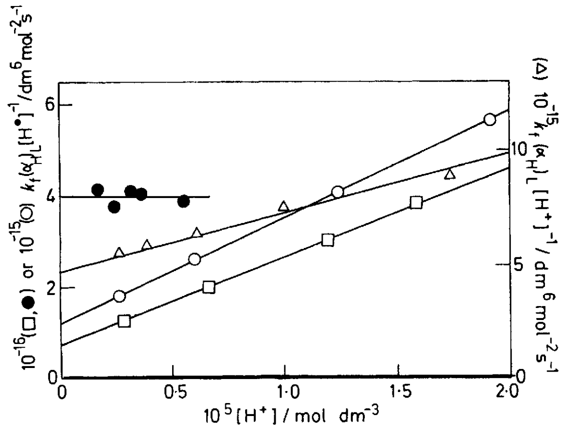

FIGURE 3 Plots of $k_f(\alpha_H)_L/[H^+]$ against $[H^+]$ for reactions of Zn^{II} with: (○) L^1 at c_{Zn} = 4.81 × 10^{-4}, c_L = 4.09 × 10^{-4}, and $[MeCO_2^-]$ = 0.05 mol dm^{-3}; (△) L^2 at c_{Zn} = 2.89 × 10^{-4}, c_L = 3.85 × 10^{-4}, and $[MeCO_2^-]$ = 0.10 mol dm^{-3}; (□) L^3 at c_{Zn} = 2.89 × 10^{-4}, c_L = 3.85 × 10^{-4}, and $[MeCO_2^-]$ = 0.10 mol dm^{-3}; and (●) L^4 at c_{Zn} = 1.0 × 10^{-4}, c_L = 2.0 × 10^{-4}, and $[MeCO_2^-]$ = 0.05 mol dm^{-3}

Kinetic Studies.—The complex formation between the

TABLE 5

Initial rate data for complex formation of metal(II) ions with macrocyclic tetra-amines at I = 0.20 mol dm^{-3}

10^3c_M [a]	10^3c_L [a]	pH	$[MeCO_2^-]$ [a]	k_f [b]	$\frac{k_f\beta_{MeCO_2}}{[MeCO_2^-]K_{M(O_2CMe)}}$ [b]
Zn^{II}–L^1 (at 25 °C)					
0.481	0.205	5.22	0.10	2.9	
	0.409	5.22	0.10	2.9	9.3
	0.818	5.22	0.10	2.9	
	1.636	5.22	0.10	2.9	
0.120	0.818	5.22	0.10	2.8	
0.241	0.818	5.22	0.10	2.9	
0.962	0.818	5.22	0.10	3.0	
0.481	0.409	5.22	0.025	0.95	9.3
	0.409	5.22	0.050	1.7	9.3
	0.409	5.22	0.20	4.4	9.2
Zn^{II}–L^2 (at 25 °C)					
0.289	0.385	5.40	0.10	9.4	30
	0.770	5.40	0.10	9.4	
	1.540	5.40	0.10	9.4	
0.145	0.385	5.40	0.10	9.4	
0.578	0.385	5.40	0.10	9.4	
0.289	0.385	5.40	0.03	3.8	30
	0.385	5.40	0.05	5.6	30
	0.385	5.40	0.20	14	30
Zn^{II}–L^3 (at 25 °C)					
0.289	0.386	5.18	0.10	0.61	1.9
	0.772	5.18	0.10	0.61	
	1.544	5.18	0.10	0.61	
0.145	0.772	5.18	0.10	0.60	
0.578	0.772	5.18	0.10	0.61	
0.867	0.772	5.18	0.10	0.61	
0.289	0.386	5.18	0.030	0.23	1.9
	0.386	5.18	0.050	0.36	1.9
	0.386	5.18	0.20	0.93	2.0
Zn^{II}–L^4 (at 10 °C)					
0.10	0.10	5.50	0.05	6.6	
	0.20	5.50	0.05	6.5	30
	0.40	5.50	0.05	6.6	
	0.60	5.50	0.05	6.5	
	1.00	5.50	0.05	6.6	
0.20	0.20	5.50	0.05	6.6	
0.30	0.20	5.50	0.05	6.5	
0.10	0.20	5.50	0.03	3.6	30
	0.20	5.50	0.10	11	31
	0.20	5.50	0.20	16	31
	0.20	5.28	0.05	3.7	
	0.20	5.44	0.05	5.6	
	0.20	5.62	0.05	8.0	
	0.20	5.77	0.05	12	
Pb^{II}–L^1 (at 27 °C unless otherwise noted)					
0.240	0.192	4.91	0.10	23	
	0.386	4.91	0.10	23	
	0.576	4.91	0.10	24	
0.120	0.386	4.91	0.10	23	
0.360	0.386	4.91	0.10	24	
0.240	0.386	5.20	0.05	39	50
	0.386	5.20	0.10	36	50
	0.386	5.20	0.20	30	50
	0.385	4.67	0.10	10 [c]	
	0.385	4.90	0.10	12 [c]	
	0.383	5.20	0.10	19 [c]	
	0.383	5.40	0.10	25 [c]	
Cd^{II}–L^1 (at 25 °C)					
0.10	0.468	5.20	0.10	7.7	
0.20	0.468	5.20	0.10	7.8	
0.30	0.468	5.20	0.10	7.6	
0.10	0.234	5.20	0.10	7.7	13
	0.702	5.20	0.10	7.8	
	0.234	5.20	0.05	5.8	13
	0.234	5.20	0.20	9.3	13
	0.234	4.78	0.10	3.7	
	0.234	4.94	0.10	4.9	
	0.234	5.51	0.10	15	

[a] Units mol dm^{-3}. [b] Units dm^3 mol^{-1} s^{-1}. [c] At 21 °C.

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* Throughout this paper: 1 cal = 4.184 J.

[18] C. N. Reilley and R. W. Schmid, *J. Elisha Mitchell Sci. Soc.*, 1957, **73**, 279.

metal(II) ions and the macrocycles occurred at measurable rates in acetate buffers and the apparent second-order rate constants, k_f, were determined by the initial-gradient method. Typical results at a given pH are shown in Table 5. At a given concentration of $[MeCO_2]^-$, plots of $k_f(\alpha_H)_L/[H^+]$ against $[H^+]$ were linear with finite intercepts for all the reactions (Figures 3—5). These effects of $[MeCO_2^-]$ and $[H^+]$ on k_f were identical to those found for the copper(II) system.[2,4,5] The kinetics were examined at several temperatures (15—35 °C) in order to construct Arrhenius plots and hence determine the activation parameters.

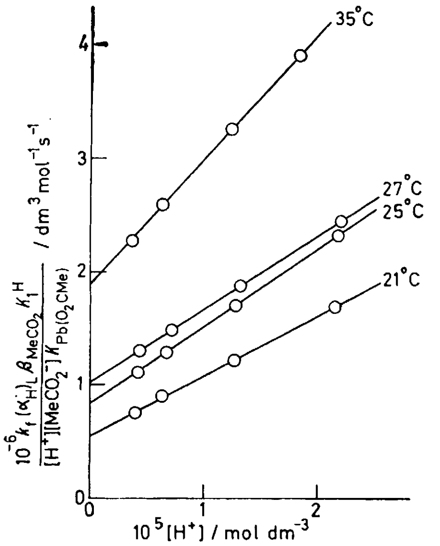

FIGURE 4 Plots of $10^{-6}k_f(\alpha_H)_L\beta_{MeCO_2}K_1^H/[H^+]K_{Pb(O_2CMe)}$-$[MeCO_2^-]$ against $[H^+]$ for reaction of Pb^{II} and L^1 at $c_{Pb} = 2.40 \times 10^{-4}$, $c_L = 3.85 \times 10^{-4}$, $[MeCO_2^-] = 0.10$, and $I = 0.20$ mol dm^{-3}

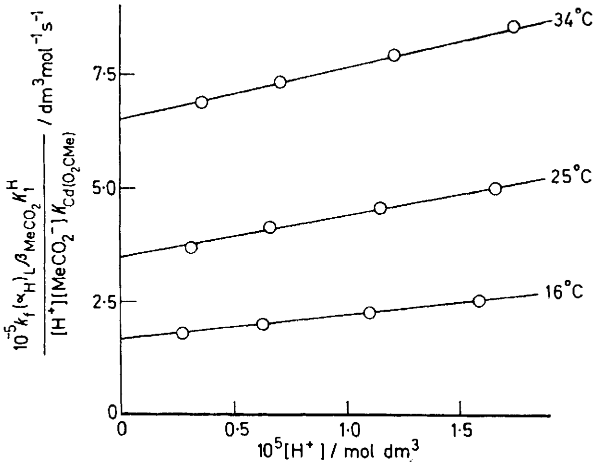

FIGURE 5 Plots of $10^{-5}k_f(\alpha_H)_L\beta_{MeCO_2}K_1^H/[H^+]K_{Cd(O_2CMe)}[MeCO_2^-]$ against $[H^+]$ for reaction of Cd^{II} and L^1 at $c_{Cd} = 1 \times 10^{-4}$, $c_L = 2.34 \times 10^{-4}$, $[MeCO_2^-] = 0.10$, and $I = 0.20$ mol dm^{-3}

DISCUSSION

Stability of the Zinc(II) *Macrocycles*.—The high stability of the 1 : 1 complexes of Zn^{II} with the 12- to 15-membered macrocyclic tetra-amines is evident.* The formation constants are several orders of magnitude larger than those for corresponding linear homologues L^5,L^6, 4,7-diazadecane-1,10-diamine (L^7), and 4,8-diazaundecane-1,11-diamine (L^8) [19] (see Table 2). Thus, the macrocyclic effects known for Cu^{II} (refs. 1—5, 7, 8, and 20) and Ni^{II} (refs. 14, 16, 21, and 22) are also evident for Zn^{II}. It is of interest that these metal ions are all small with sizes (ionic radii: Cu^{II}, 0.72; Ni^{II}, 0.69; and Zn^{II}, 0.74 Å) [23] comparable to the macrocyclic cavities.[12]

The extra stability of the 12- to 15-membered macrocyclic complexes of Zn^{II} arises from the entropy term with the enthalpy having a slightly negative contribution. This was the case with Cu^{II}–L^1 and an essentially similar interpretation can be applied to the present macrocyclic effect: a favourable orientation of the macrocyclic ligands before chelation due to steric requirements and probably decreased complex solvation in the outer sphere.[1,2] The situation is somewhat similar to the recently reported entropy-controlled formation of a zinc(II) complex with 1,3,5-*cis*,*cis*-triaminocyclohexane.[24] In contrast to the present macrocyclic effects are those which arise entirely (as in Ni^{II}–L^3) [14,21] and partially (as in Cu^{II}–L^2, [3,4] Cu^{II}–L^3, [25] or Cu^{II}–L^4) [5] from the enthalpy term. An explanation given for the former case deals with the ligand-solvation effects,[14,21] while that for the latter is the increased Cu–N bond strength due to the ligand cyclization.[25]

Zinc(II) differs from Cu^{II} in that the enthalpy changes on complex formation are almost the same regardless of the ring size of the macrocycle. With copper complexes of linear tetra-amine ligands (L^5—L^8) the effects of alternating five- and six-membered chelate rings on complex stability are well demonstrated.[19,26] Planar complexes are expected to be considerably stabilized by such a sequence of the chelate rings due to the removal of ' girdle strain '.[27] This stabilization is reflected in the greater heat of formation arising from the stronger Cu–N bond.[28] The same effect occurs in the copper macrocyclic complexes; among 12- to 15-membered systems, Cu^{II}–L^3, having alternatively five- and six-membered chelate rings, shows the largest $-\Delta H$ value which is

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* Using the present experimental method, we observed neither complex isomerization (as seen for the copper(II) complex of methyl-substituted L^3) [7] nor protonation of the co-ordinated macrocycles (as seen for Cu^{II}–L^4).[5]

[19] R. Barbucci, L. Fabbrizzi, P. Paoletti, and A. Vacca, *J.C.S. Dalton*, 1973, 1762 and refs. therein.

[20] T. E. Jones, L. L. Zimmer, L. L. Diaddario, D. B. Rorabacher, and L. A. Ochrymowycz, *J. Amer. Chem. Soc.*, 1975, **97**, 7163.

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[26] P. Paoletti, L. Fabbrizzi, and R. Barbucci, *Inorg. Chem.*, 1973, **12**, 1861.

[27] R. Barbucci, L. Fabbrizzi, and P. Paoletti, *Co-ordination Chem. Rev.*, 1972, 8.

[28] L. Fabbrizzi, P. Paoletti, and A. B. P. Lever, *Inorg. Chem.*, 1976, **15**, 1502 and refs. therein.

probably due to it having the strongest Cu–N bond,[25] as supported by the highest $\nu(d\text{–}d)$ frequency in the visible region.[28] This behaviour was anticipated from conformational analysis of the square-planar macrocyclic complexes.[12] In tetrahedral complexes, on the other hand, the strength of the metal–donor interaction would be less affected by this sort of strain release. The approximately constant enthalpy values (*ca.* -8 kcal mol^{-1}) for all the zinc(II) macrocycles strongly suggest that the geometry of these complexes is tetrahedral. This is not surprising in view of the well known preference of Zn^{II} for tetrahedral co-ordination. A similar $-\Delta H$ value (8.9 kcal mol^{-1}) for Zn^{II}–L^5 (a typical four-co-ordinate tetrahedral complex)[29] provides supporting evidence. The entropy term for the zinc macrocyclic complexes is also characteristic. The narrow range for L^1—L^4 somewhat parallels the case for the linear homologues L^5—L^8. This may reflect parallel freezing of the conformational freedom of the ligands and similar effects of desolvation and solvation accompanying tetrahedral complex formation with L^1—L^4.

Stability of the Cadmium(II) *and Lead*(II) *Macrocycles*.—It is of interest that among L^1—L^4, only L^1, which has the smallest N_4 cavity, forms a stable complex with the large metal ions Cd^{II} (ionic radius 0.97 Å) and Pb^{II} (1.20 Å) in acetate buffer solutions. In terms of fitting the metal ion into the cavity, L^1 is the least preferred macrocycle. However, one assumes that the diminished stability of complexes having alternate five- and six-membered rings (*e.g.* Pb^{II}–L^6) relative to those having all five-membered rings (*e.g.* Pb^{II}–L^5) is translated into the macrocyclic system, just as it is for mercury(II) complexes.[6] Together with the zinc(II) study, it may be argued that cavity size is not a determining factor in d^{10} metal-ion complexes of macrocyclic tetra-amines, as it is for Cu^{II}.[1-5]

The 1 : 1 Cd^{II}– and Pb^{II}–L^1 complexes are 10^4—10^5 times more stable than the corresponding complexes of the related linear ligand L^5. Further, the cyclization effects for these large metal ions are commonly characterized by a minor enthalpy loss and an enormous entropy gain. It is now clear that the cause of the macrocyclic effect is the same for Cu^{II},[1,2] Zn^{II}, Cd^{II}, and Pb^{II}. The complexes of Cd^{II} and Pb^{II} contrast with that of Hg^{II} where the comparably sized metal ion (1.10 Å) receives little benefit from ligand cyclization, owing to a large enthalpy loss dominating the entropy gain [$\Delta(\Delta S)$ 27 cal K^{-1} mol^{-1}].[6] The complex of Hg^{II} may be exceptional in that the favourable preorientation is nullified by a drastic alteration in the co-ordination number or geometry.

Kinetics of Macrocyclic Complex Formation.—The rate constants for formation of the macrocyclic complexes of Zn^{II}, Cd^{II}, and Pb^{II} were measured in acetate buffers. Under more acidic conditions there was little complex formation. At pH >6 using other buffers, the reactions were too fast to be followed with the polarographic technique. In acetate buffers, the same rate law (5) can be formulated as that for Cu^{II},[1-5] where k_H and k_{2H}

$$k_f(\alpha_H)_L \frac{\beta_{MeCO_2}}{K_{M(O_2CMe)}[MeCO_2^-]} = \frac{k_H[H^+]}{K_1^H} + \frac{k_{2H}[H^+]^2}{K_1^H K_2^H} \qquad (5)$$

are the rate constants for the reactions of $[M(O_2CMe)]^+$ with $[HL]^+$ and $[H_2L]^{2+}$, which can be determined from the linear plots in Figures 3—5. For Zn^{II}–L^4, the gradient found is approximately zero, as for Cu^{II}–L^4, which means that the contribution of $[H_2L]^{2+}$ to the net reaction rate can be ignored. However, this does not necessarily mean that the k_{2H} values are smaller than those for other macrocycles. Even if $k_{2H} \approx 5$ dm^3 mol^{-1} s^{-1} its contribution to the net rate at pH 5.5 would be *ca.* 5%, which might not be experimentally detected. All the kinetic data based on this interpretation are summarized in Table 6. It is to be noted that expression (5) can represent a number of kinetically indistinguishable processes: the reactants involved might take other forms such as those arising from acid ionization of aquametal ions. The discussion which follows assumes the same processes to be occurring for Cu^{II} and the present metal ions.

TABLE 6

Comparison of rate constants k_H and k_{2H} and the associated activation parameters for reactions of metal(II) ions with macrocyclic tetra-amines at I 0.20 mol dm^{-3} and 25 °C

Reaction	k_H [k_{2H}] dm^3 mol^{-1} s^{-1}	$\Delta H^‡$ kcal mol^{-1}	$\Delta S^‡$ cal K^{-1} mol^{-1}
$Zn^{II} + L^1$	$(1.3 \pm 0.1) \times 10^5$	14.3 ± 0.3]	9 ± 2
	[3.9 ± 0.2]	[18.0 ± 0.3]	[1 ± 1]
$Zn^{II} + L^2$	$(1.2 \pm 0.1) \times 10^6$	13.0 ± 0.3	9 ± 2
	[5.1 ± 0.2]	[18.9 ± 0.3]	[3 ± 1]
$Zn^{II} + L^3$	$(7.5 \pm 0.5) \times 10^4$	14.9 ± 0.3	10 ± 2
	[1.0 ± 0.1]	[18.0 ± 0.3]	[−2 ± 1]
$Zn^{II} + L^4$	$(4.5 \pm 0.5) \times 10^6$	13.7 ± 0.6	14 ± 4
$Pb^{II} + L^1$	$(8.3 \pm 0.1) \times 10^5$	14.6 ± 0.3	23 ± 2
	[1.4 ± 0.2]	[17.1 ± 0.3]	[5 ± 1]
$Cd^{II} + L^1$	$(3.5 \pm 0.1) \times 10^5$	14.3 ± 0.3	15 ± 2
	[1.8 ± 0.2]	[18.1 ± 0.3]	[4 ± 1]

The rate constants (k_H) and the activation parameters for the reactions of $[HL]^+$ with Zn^{II} do not drastically vary with the size of the macrocycles, indicating basically that the same reaction mechanism is operating. A similar trend was seen for Cu^{II}.[1-5,25] The relative rates (at 25 °C) for Zn^{II} and Cu^{II} are 7.2×10^{-2}, 2.5×10^{-1}, 1.6×10^{-2}, and 1.3×10^{-2} with L^1, L^2, L^3, and L^4, respectively. For the reactions between Cu^{II} and $[HL]^+$, the rate constants and activation parameters for L^2 and L^3 are almost the same as those for the reactions measured at more acidic pH values without inclusion of the acetate anions, indicating that the presence of acetate anions has little kinetic effect.[4,25] Further, an analysis of the reaction of $[HL]^+$ species with Cu^{2+}(aq) suggested that the rate-determining step is most likely the dissociation of water prior to the first co-ordinate bond formation ('dissociative mechanism').[4,25] Now, the relative rate of water exchange for Zn^{2+}(aq) and Cu^{2+}(aq) is 1.6×10^{-2}.[30] Therefore, the close parallel with the relative rate constants (k_H) for Zn^{II} and Cu^{II}

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[29] L. Sacconi, P. Paoletti, and M. Ciampolini, *J. Chem. Soc.*, 1961, 5115.

(L^2 deviates slightly for unknown reasons) suggests that water dissociation is also the rate-determining step for the reactions of Zn^{II} and $[HL]^+$. Of interest is the report[31] that the reaction of a methyl-substituted L^2 with Zn^{II} (measured by a pH-stat method) gives a rate constant for the monoprotonated ligand species of 8.0×10^4 mol dm^{-3} s^{-1} (I 0.5 mol dm^{-3} and 25 °C), not greatly different from our values for the relevant species. The stability constants of $[M(O_2CMe)]^+$ (log-$K_{M(O_2CMe)}$ 1.72 for Cu and 0.66 for Zn)[15] do not seem to perturb the relation between the water-exchange and ligand-substitution rates. For the 15-membered ring, the constraint of the cyclic structure probably decreases thus increasing the distance between the protonated site and a metal ion approaching an unprotonated donor site, and also increasing the ligand conformational flexibility. This should increase otherwise low K_0 and/or k_0 values in the Eigen mechanism,* which may be a reason for the faster complexation rate for L^4 than the smaller macrocyclic ligands. This trend in the complexation rate is observed for some acyclic ligands.[30]

The magnitudes of k_H for the large metal ions Cd^{II} and Pb^{II} are not particularly unusual, and moreover the ratio of k_H to k_{-H_2O} (the water-exchange rate of the aquated metal ion)[30] for Pb^{II} ($10^{-3.4}$: 1) and for Cd^{II} ($10^{-3.1}$: 1) almost parallels those for Zn^{II} ($10^{-2.4}$: 1) and Cu^{II} ($10^{-3.0}$: 1). These facts, together with the positive $\Delta S^‡$, may imply that the rate-determining step of the macrocyclic complex is water dissociation regardless of the size of the metal ions. Interestingly, similar orders of the $k_H : k_{-H_2O}$ ratio, 10^{-3}—10^{-4} : 1, were reported for the reactions between methyl-substituted L^2 or L^3 and Ni^{II}, Cu^{II}, Co^{II}, and Zn^{II}.[31,32] As discussed before, the practically invariable $k_H : k_{-H_2O}$ values for all the tested metal ions may mean that for Cd and Pb the effects of acetate anions on the k_H values are as negligible as for Zn and Cu.

The reactions of $[H_2L]^{2+}$ with the d^{10} metal ions proceed too slowly relative to those of $[HL]^+$ to be explained solely by electrostatic effects, and a different transition state might be considered as for Cu^{II}.[2,4] The proton-transfer step aided by the acetate anions may become rate-limiting for these metal ions, too. The acetate anion, acting probably as a base, accelerates the reactions of Cu^{II} and $[H_2L]^{2+}$ by a factor of *ca.* 100.[4,25]

[7/139 *Received, 26th January, 1977*]

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* On the basis of the equation $k_f = K_0 k_0$, where K_0 is the outer-sphere association constant and k_0 is the rate constant for breakdown of the outer- to the inner-sphere complex (M. Eigen and K. Tamm, *Z. Electrochem.*, 1962, **66**, 107).

[30] R. G. Wilkins, 'The Study of Kinetics and Mechanism of Reactions of Transition Metal Complexes,' Allyn and Bacon, Boston, 1974, p. 219.

[31] W. Steinmann and T. A. Kaden, *Helv. Chim. Acta*, 1975, **58**, 1358.

[32] L. Hertli and T. A. Kaden, *Helv. Chim. Acta*, 1974, **57**, 1328.