Zinc(II) Complexes of Dipropylenetriamine and *N*-(2-Aminoethyl)propane-1,3-diamine: A Carbon-13 Nuclear Magnetic Resonance Study†

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Carbon-13 n.m.r. spectra are reported as a function of pH for mixtures of dipropylenetriamine (dpt) or *N*-(2-aminoethyl)propane-1,3-diamine (aepn) and zinc nitrate, of zinc and dpt or aepn with 1,2-diaminoethane (en), 1,3-diaminopropane (pn), and glycine (gly), and of zinc and aepn with L-alanine (ala), β-alanine (β-ala), and *trans*-1,2-diaminocyclohexane (dach). Carbon-13 chemical shifts are also reported as a function of pH for dpt, β-ala, and dach alone. The pH profiles have been analysed by computer and chemical shifts determined for the following species: dpt, $Hdpt^+$, H_2dpt^{2+}, H_3dpt^{3+}, β-alaO, β-ala, dach, $Hdach^+$, H_2dach^{2+}, $[Zn(dpt)]^{2+}$, $[Zn(dpt)(Hdpt)]^{3+}$, $[Zn(dpt)_2]^{2+}$, $[Zn(dpt)(OH)]^+$, $[Zn(dpt)(en)]^{2+}$, $[Zn(dpt)(glyO)]^+$, $[Zn(aepn)]^{2+}$, $[Zn(aepn)(Haepn)]^{3+}$, $[Zn(aepn)_2]^{2+}$, $[Zn(aepn)(OH)]^+$, $[Zn(aepn)(en)]^{2+}$, $[Zn(aepn)(pn)]^{2+}$, $[Zn(aepn)(dach)]^{2+}$, $[Zn(aepn)(glyO)]^+$, $[Zn(aepn)(alaO)]^+$, and $[Zn(aepn)(\beta\text{-alaO})]^+$. Stability constants have also been determined for the bis and ternary complexes. Potentiometric titrations with dpt, zinc + dpt, and zinc + aepn solutions provide support for the interpretation of the chemical shift data. The results are compared with those of a previous study with diethylenetriamine and used to provide evidence concerning the co-ordination geometry of zinc in these complexes.

The prominent position occupied by zinc(II) in enzyme chemistry is associated with its ability to adopt a co-ordination number of four, five, or six,[1] yet its d^{10} configuration makes it particularly difficult to study in solution and most zinc stability constants have been determined[2] by non-specific methods (such as potentiometry) where ambiguity sometimes exists over the interpretation of the data. We have shown[3] that ^{13}C n.m.r. spectroscopy may be used to identify the separate complexes in a zinc–organic ligand mixture and now report the use of this method to identify and characterise the major zinc complexes present in aqueous solutions containing one of the linear triamines *N*-(2-aminoethyl)propane-1,3-diamine (aepn) or 4-azaheptane-1,7-diamine (dipropylenetriamine, dpt). Our main reasons for choosing these ligands were an inability to rationalise our temperature-jump kinetic data for ternary complex formation[4] in terms of the published stability constants and a realisation, from our recent study[5] with the homologue 3-azapentane-1,5-diamine (diethylenetriamine, dien), that the formation of important species might have been overlooked in earlier investigations[6–8] (which, in any case, differ significantly in their conclusions). We provide ^{13}C n.m.r. data and supporting potentiometric evidence which confirm the formation of bis and hydroxy complexes {$[ML_2]$ and $[ML(OH)]$} with both amines; in addition, we find that with aepn and dpt, as with dien, the protonated bis(complex) $[ML(HL)]^{3+}$ is important in the weakly alkaline region.

The second purpose of the present paper is to report the use of the ^{13}C n.m.r. technique to characterise the ternary complexes formed in solutions containing zinc, either aepn or dpt, and one of a series of potentially bidentate ligands, A. In our studies with triethylenetetramine (trien),[3,9] 2,2′,2″-triaminotriethylamine (tren),[10] and 3,7-diazanonane-1,9-diamine (dadn),[11] as well as that with dien,[5] we found that the identities of the analogous ternary complexes formed and the values of their chemical shifts provided useful evidence about the co-ordinational preference of zinc when bound to these ligands: it was our aim to draw similar conclusions about its co-ordination with aepn and dpt. From the present and previous[5] data, it is argued that the metal normally adopts a trigonal-bipyramidal arrangement with each of the triamines (dien, aepn, or dpt), with the secondary nitrogen in the axial position. In the (unprotonated) bis(complexes), however, the co-ordination number rises to six and a *mer*-octahedral configuration results.

Experimental

4-Azaheptane-1,7-diamine (Fluka; b.p. 75 °C at 0.05 Torr) and *trans*-1,2-diaminocyclohexane (Aldrich; b.p. 38—50 °C at 0.05 Torr) were purified by distillation, and β-alanine (Aldrich; Gold Label 99 + %) was used without further purification. The other chemicals were purified, and the solutions made up in D_2O as described previously;[12,13] pD = pH meter reading + 0.40. The n.m.r. spectra were recorded[12,13] at 21 ± 1 °C with a JEOL FT-100 instrument, using air-conditioning and compressed air to achieve thermostatting. Chemical shifts were measured relative to internal 1,4-dioxane (δ 67.71) and are quoted on the δ scale; they are estimated to be reliable to ±0.12 p.p.m. when taken from a spectrum which includes a carboxylate resonance, otherwise to ±0.04 p.p.m. The potentiometric titrations were performed[13] under a CO_2-free atmosphere using initial volumes of 5.70 cm³ and [NaOH] = 0.98 mol dm⁻³. The analysis was performed as described previously[5,12,13] and, as in recent papers, we have indicated the quality of fit of the pD profiles by the standard deviations calculated from the difference between the observed δ values and those computed on the basis of the parameters listed.

Results

1. *The Free Ligands.*—The C atoms in pn, dach, alaO, β-alaO, dpt, and aepn are identified as follows:

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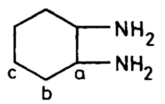
† *Supplementary data available* (No. SUP 56716, 8 pp.): observed chemical shifts for solutions containing dpt and aepn. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1988, Issue 1, pp. xvii—xx.

The notation used in this paper is similar to that used previously: L = dpt or aepn; ligand X = A (glyO, alaO, β-alaO, en, pn, or dach) or HA (gly, ala, Hpn^+); gly = glycine, glyO = glycinate(1 −), ala = L-alanine, alaO = L-alaninate(1 −), β-ala = β-alanine, β-alaO = β-alaninate(1 −), en = 1,2-diaminoethane, pn = 1,3-diaminopropane, dach = *trans*-1,2-diaminocyclohexane.

pn	$NH_2C_aH_2C_bH_2CH_2NH_2$
dach	
alaO	$C_aH_3C_bH(NH_2)CO_2^-$
β-alaO	$NH_2C_aH_2C_bH_2CO_2^-$
dpt	$(NH_2C_aH_2C_bH_2C_cH_2)_2NH$
aepn	$NH_2C_aH_2C_bH_2NHC_cH_2C_dH_2C_eH_2NH_2$

The measured chemical shifts, δ, for the C atoms in dpt, dach, and β-ala at different pD are represented by the triangles in Figures 1, 2(*d*), and 2(*e*). The dashed titration curves in Figures 1, 2, and 3 were computed from these data and others obtained previously, using the pK_a values (pK_D^c) and individual chemical shifts listed in Table 1. The assignment[13] of the C_b and C_c resonances of aepn at low pD, while agreeing with that of Delfini *et al.*,[14] differs from that made initially.[12] The reason for the change is that the low-pD part of the profile for the Zn + aepn system (see below) computed on the basis of the original assignment deviated to an unacceptable extent from the experimental points. It would appear that, as in the case of the analogous carbon atoms C_b and C_c in dadn,[11] the size of the cross-term needed for C_b was originally underestimated.[12]

The spectral assignments for dpt were made as described in ref. 12 and those for dach using published[15] substituent chemical shifts for cyclohexanes, which gave predicted values of 60.8, 35.4, and 24.5 p.p.m., respectively, for C_a, C_b, and C_c in the unprotonated form. The two methylene carbons in β-ala were assigned using the large protonation shift of C_b which is characteristic of a β-electric field interaction[16] and the failure to obtain a satisfactory computed fit to the experimental points with the alternative non-crossing assignment. In all three cases the spectral lines were sharp throughout, with relative heights consistent with rapid exchange between the various protonated forms.

The derived pK_D^c values for β-ala and dach (Table 1) are in good agreement with the literature values in H_2O (pK_H^c = 10.17,[17] and 9.89, 6.72,[18] respectively) if a typical value of 0.6 is

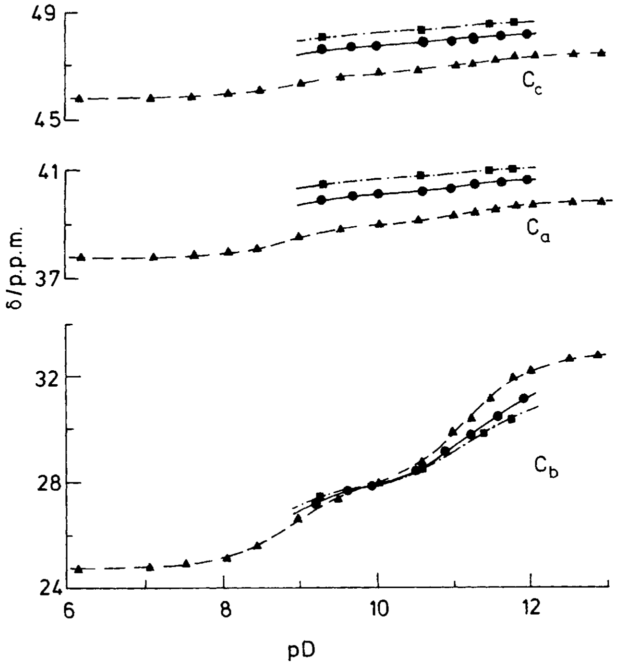


Figure 1. ^{13}C N.m.r. chemical shifts as a function of pD for dpt (0.20 mol dm^{-3}, ▲) and zinc + dpt (0.05 + 0.22 mol dm^{-3}, ●; or 0.05 + 0.15 mol dm^{-3}, ■)

Table 1. 'Best' ^{13}C chemical shift (in p.p.m.) and pK_a values (pK_D^c) for free ligands

Ligand[a]		δ(Y)	δ(HY)	δ(H_2Y)	δ(H_3Y)	pK_D^c
dpt[b]	C_a	39.85	39.02	39.08	37.78	11.20, 10.54, 8.87
	C_b	32.90	28.60	28.00	24.77	
	C_c	47.42	46.73	46.70	45.82	
aepn[c]	C_a	41.00	39.70	39.60	36.55	10.75, 10.02, 6.96
	C_b	52.10	49.90	47.10	45.45	
	C_c	47.30	46.80	46.60	46.15	
	C_d	32.75	27.90	27.30	24.75	
	C_e	39.80	39.00	38.90	37.65	
en[d]		43.98	40.86	37.64		10.76, 7.95
pn[d]	C_a	39.38	38.82	37.76		11.15, 9.65
	C_b	36.00	30.80	25.97		
gly	CH_2	45.85[c]	42.60[c]			10.37[c]
	CO_2^-	182.70[e]	173.40[e]			
ala	C_a	21.54[c]	17.27[c]			10.46[c]
	C_b	52.57[c]	51.66[c]			
	CO_2^-	185.72[f]	176.80[f]			
β-ala[g]	C_a	39.07	37.65			10.70
	C_b	41.65	34.60			
	CO_2^-	182.77	179.40			
dach[g]	C_a	57.30	55.70	53.40		10.60, 7.40
	C_b	34.65	33.00	30.45		
	C_c	25.95	25.10	23.93		

[a] Y = L (dpt or aepn) or A (en, pn, gly, ala, β-ala, or dach). [b] The 'best' values were determined from 16 sets of data points. The standard deviations of the experimental chemical shifts from the values calculated on the basis of the parameters listed are: C_a 0.046, C_b 0.082, and C_c 0.038. The estimated errors in δ are ±0.1 p.p.m. and in pK_D^c ±0.1. Temperature 21 ± 1 °C; *I* various. [c] Data from ref. 13. [d] Data from ref. 9. [e] Data from ref. 5. [f] Data from ref. 10. [g] Temperature 21 ± 1 °C; *I* various. The estimated errors in δ are ±0.1 p.p.m. and in pK_D^c ±0.1.

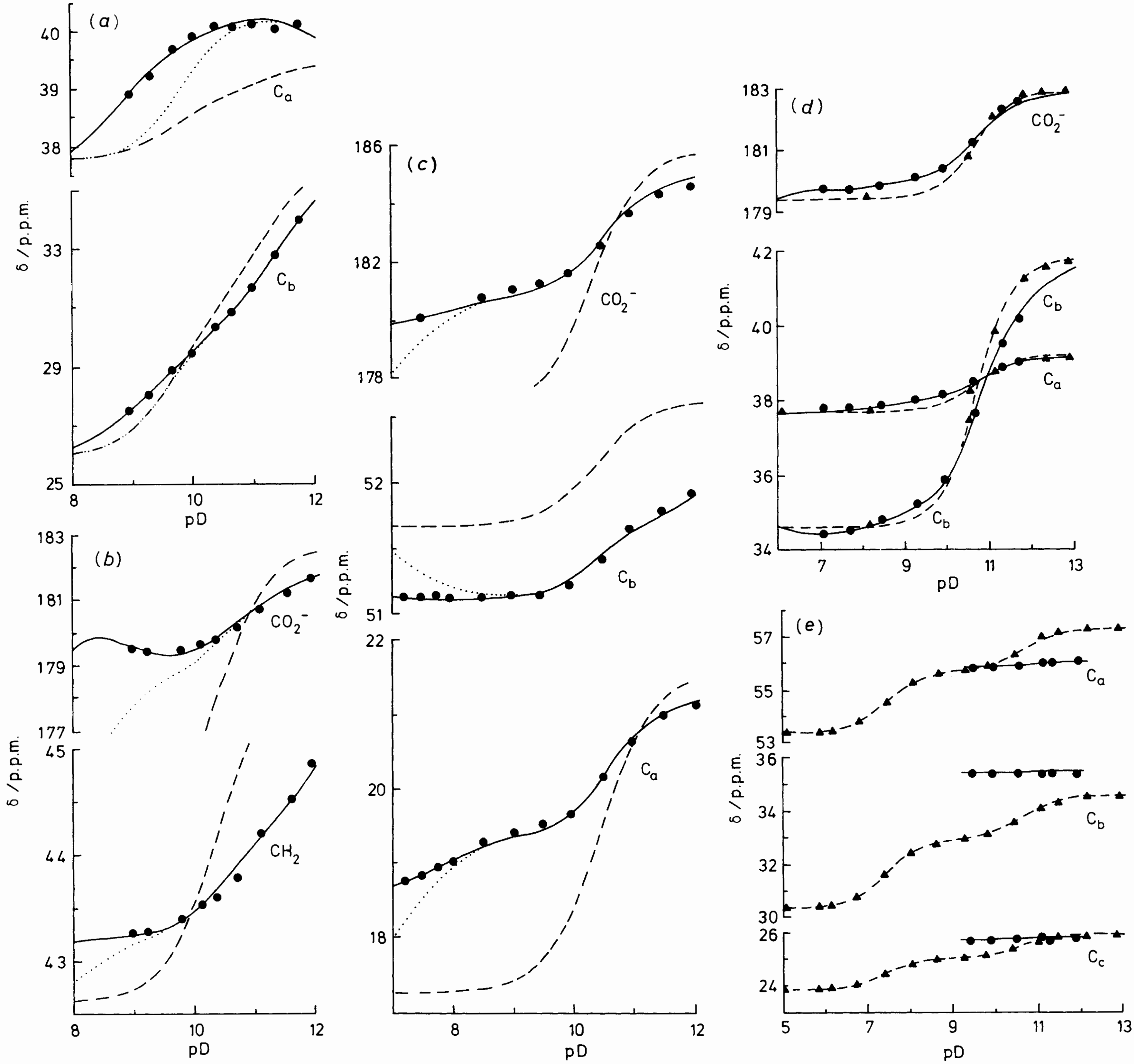


Figure 2. ^{13}C N.m.r. chemical shifts as a function of pD for β-ala [0.20 mol dm^{-3}; ▲ in (*d*)] and dach [0.10 mol dm^{-3}; ▲ in (*e*)] and for X in Zn(NO$_3$)$_2$ + dpt [(*a*) and (*b*)] or aepn [(*c*)—(*e*)] + X (●): (*a*) pn; (*b*) gly; (*c*) ala; (*d*) β-ala; (*e*) dach. Concentrations were, respectively, 0.10 + 0.20 + 0.10 mol dm^{-3} for (*a*), (*b*), and (*e*), and 0.20 + 0.40 + 0.20 mol dm^{-3} for (*c*) and (*d*)

assumed[13] for the deuterium isotope effect ΔpK ($=pK_D^c - pK_H^c$). With dpt the agreement for two of the three protonation steps is less good: applying a ΔpK of 0.6 to the average pK_H^c values of Vacca *et al.*[8] and Arishima *et al.*[7] (25 °C; I = 0.1 mol dm^{-3}) gives pK_D^c values of 11.30, 10.19, and 8.32. To confirm our pK_D^c values for dpt, we performed a potentiometric titration in D$_2$O and obtained the data shown by the triangles in Figure 4. The dashed 'best-fit' line was computed on the basis of pK_D^c values of 11.39, 10.54, and 8.78, and the good agreement between these and the ^{13}C n.m.r.-derived values given in Table 1 reinforces the view that the deuterium isotope effects for the addition of the second and third protons to dpt are anomalously large. In fact, although ΔpK is[13] typically around 0.6, quite large variations have been reported[19] and we have recently found small[5] and even negative[20] values. In our previous investigation[13] with free aepn we argued that the protonated forms should be treated as hybrid rather than multiply charged ions when determining their contributions to the ionic strength

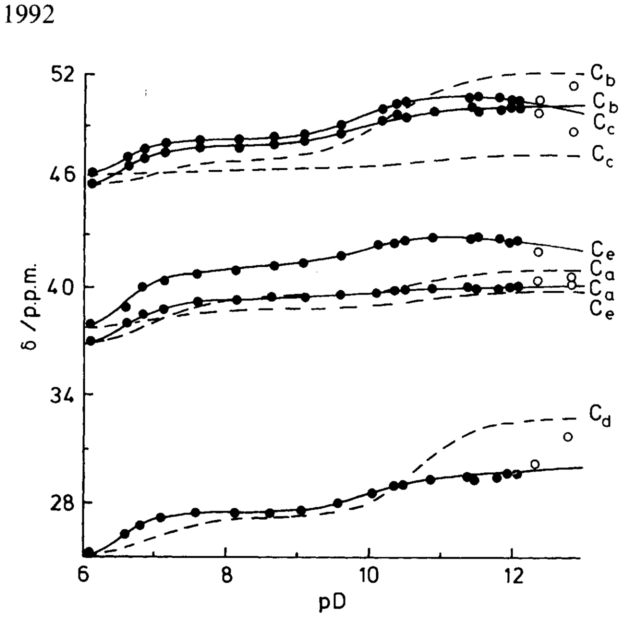


Figure 3. ^{13}C N.m.r. chemical shifts as a function of pD for zinc + aepn (0.20 + 0.40 mol dm^{-3})

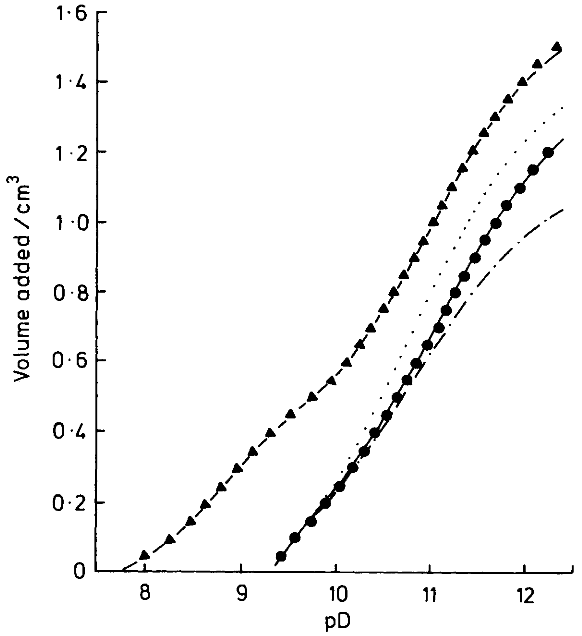


Figure 4. Potentiometric titration of dpt (0.088 mol dm^{-3}; ▲) and zinc + dpt (0.044 + 0.132 mol dm^{-3}; ●) in D_2O. NaOD (0.98 mol dm^{-3}) was added to 5.70 cm^3 of the solution

and that, as a consequence, the ionic strengths of the solutions (and therefore the mean ionic activity coefficient $\gamma_{\pm}$) vary little during the titrations. Further support for this conclusion is provided by the closeness of fit between the computed curve and the experimental points (Figure 4) over the whole pD range studied.

2. *The Binary Systems.*—(*i*) Zn^{2+} + dpt. The measured chemical shifts for Zn + dpt (0.05 + 0.22 mol dm^{-3}) at different pD are given by the circles in Figure 1. Additional spectra at concentrations of 0.05 and 0.15 mol dm^{-3}, respectively, gave chemical shifts indicated by the squares in Figure 1 but attempts to obtain spectra using a lower [dpt]:[Zn] and/or a pD value outside the range 9—12 resulted in either the precipitation of $Zn(OH)_2$ or extreme line broadening of the C_a and C_c resonances. In spite of this exchange broadening, attempts to resolve individual signals for the complexed and uncomplexed forms using low concentration proved unsuccessful as with some other zinc–polyamine systems.[9,11] The rather restricted pD range accessible for this system and the relatively small variation in observed chemical shift for two of the three C atoms makes the analysis difficult in the absence of further evidence on the identities of the complexes formed. Such evidence was provided by potentiometric titration in D_2O.

In most potentiometric investigations of zinc complexes, the concentrations and pH values used are both low and, under these conditions, it is difficult to obtain evidence for the formation of bis and hydroxy forms. For example, in the study of zinc + dpt by Vacca *et al.*,[8] only one of the four samples they used covered the pH range above 9.3 and that contained [Zn] and [dpt] of only 1.1×10^{-3} and 5.409×10^{-3} mol dm^{-3}, respectively. We used a starting pD of 9.34 and initial Zn^{2+} and dpt concentrations of 0.044 and 0.132 mol dm^{-3} respectively, and the observed volume of 0.98 mol dm^{-3} NaOD added *vs.* pD profile is given by the circles in Figure 4. Use of the stability constants of Vacca *et al.* ($\log K_1 = 7.92$; $\log K_{OH} = 5.23$) gives a poor fit to the data (shown by the dotted line) and it proved impossible to match the computed curve to the data on the basis of the formation of [ML] and [ML(OH)] alone. In view of the additional species [ML(HL)] and [ML_2] detected with L = dien[5] and aepn (see below), parameters for the formation of analogous complexes were added to the present refinement procedure. The 'best-fit' line (shown as the solid line in Figure 4) provides a good representation of the experimental points; it was computed using the following equilibrium constants: $\log K_1 = 7.92$, $\log K_2 = 2.48$, $\log K^{ML}_{ML(HL)} = 2.09$ {equivalent to a $pK_D{}^c$ value for [ML(HL)] of 11.00} and $pK_D{}^c$ for [ML] = 10.10. [The value of $\log K_1$ was taken from ref. 8 and the estimated errors in $\log K_2$, $\log K^{ML}_{ML(HL)}$ and $pK_D{}^c$(ML) are ± 0.3.] The low values of $\log K_2$ and $\log K^{ML}_{ML(HL)}$ confirm that the two bis complexes would be difficult to detect under the conditions used by Vacca *et al.* The dot-dashed line in Figure 4 was computed on the basis of the formation of [ML], [ML(HL)], and [ML_2] only and demonstrates the need to incorporate parameters for [ML(OH)].

The chemical shift profiles (Figure 1, solid and dot-dashed lines) were computed using the individual chemical shifts and equilibrium constants shown in Tables 1 and 2, and assuming rapid exchange of dpt throughout. The differential line broadening over the whole titration range could be explained in terms of the difference in δ values between complexed and uncomplexed forms of the ligand. For example, at pD 9.23 and [Zn] = 0.05, [dpt] = 0.22 mol dm^{-3}, the relative linewidths are C_a, $C_c \gg C_b$, whilst the corresponding approximate values of $|\delta_{free} - \delta_{complexed}|$ are 4.3, 3.9, and 0.7 p.p.m.

(*ii*) Zn^{2+} + aepn. The measured chemical shifts for Zn + aepn (0.20 + 0.40 mol dm^{-3}) at different pD are given by the points in Figure 3; additional spectra were recorded using 0.58 mol dm^{-3} aepn + 0.20 mol dm^{-3} Zn (see supplementary material, SUP 56716). All five resonances were sharp and of approximately equal intensity with the exception of some peaks (primarily those due to C_c and C_e) below pD 9 where exchange broadening occurred (see below). Given the assignments of the free ligand, it is possible to assign the lines in the rapidly exchanging ligand + complex system unequivocally. First, the resonances for the latter approach those of the free aepn system as the pD is reduced below 7 or raised above 12 (Figure 3) and the complexes dissociate (*cf.* Figure 5). Data corresponding to the high-pD dissociation (illustrated by the hollow circles) have not been treated by computer in view of the complexity of zinc

Table 2. 'Best'[a] ^{13}C chemical shifts[b] (in p.p.m.) and formation constants[c] for zinc–dpt complexes

Complex		δ(dpt)					
		C_a	C_b	C_c		δ(X)	log K^{ML}_{MLX}
$[Zn(dpt)]^{2+}$	[ML]	44.20	27.90	51.20			7.92[d]
$[Zn(dpt)(Hdpt)]^{3+}$	[ML(HL)]	41.70	27.80	49.20			2.28[e]
$[Zn(dpt)_2]^{2+}$	$[ML_2]$	42.30	29.70	49.50			2.48
$[Zn(dpt)(OH)]^+$	[ML(OH)]	43.80	28.30	51.30			10.10[f]
$[Zn(dpt)(en)]^{2+}$	[MLA]	43.60	28.20	51.00		40.80	3.40
$[Zn(dpt)(pn)]^{2+}$	[MLA]	*g*	*g*	*g*	C_a	44.20	2.18
					C_b	27.80	
$[Zn(dpt)(glyO)]^+$	[MLA]	44.30	27.30	51.70	CH_2	43.45	3.08
					CO_2^-	180.70	
$[Zn(dpt)(Hpn)]^{3+}$	[ML(HA)][h]	*g*	*g*	*g*	C_a	42.15	1.48
					C_b	29.80	
$[Zn(dpt)(gly)]^{2+}$	[ML(HA)][h]	*g*	*g*	*g*	CH_2	43.45	1.90
					CO_2^-	182.70	

[a] The 'best' values for the binary system were determined from 8 sets of data points (Zn + dpt, 0.05 + 0.22 mol dm^{-3}), with standard deviations of 0.055 (C_a), 0.093 (C_b), and 0.060 p.p.m. (C_c). For the ternary systems, the numbers of data points (in parentheses) and standard deviations (in p.p.m.) for X and L (C_a, C_b, C_c) were, respectively: en (9), 0.120, 0.054, 0.081, 0.059; pn (9) 0.053 (C_a), 0.066 (C_b), 0.084, 0.078, 0.075; gly (9) 0.057 (CH_2), 0.097 (CO_2^-), 0.042, 0.074, 0.114. [b] The estimated errors are ±0.3 p.p.m. for [ML(OH)], otherwise ±0.2 p.p.m. [c] Temperature 21 ± 1 °C; *I* various, K^{ML}_{MLX} = $[Zn(dpt)X]/[Zn(dpt)][X]$ with X = $Hdpt^+$, dpt, en, pn, glyO, Hpn^+, or gly. The estimated errors in log K^{ML}_{MLX} are ±0.2. [d] Assumed value for stability constant of $[Zn(dpt)]^{2+}$ (from ref. 8). [e] Equivalent to a pK_D^c value for [ML(HL)] of 11.00. [f] pK_D^c value for [ML]; determined potentiometrically. [g] Reliable value unobtainable. [h] Formulation uncertain.

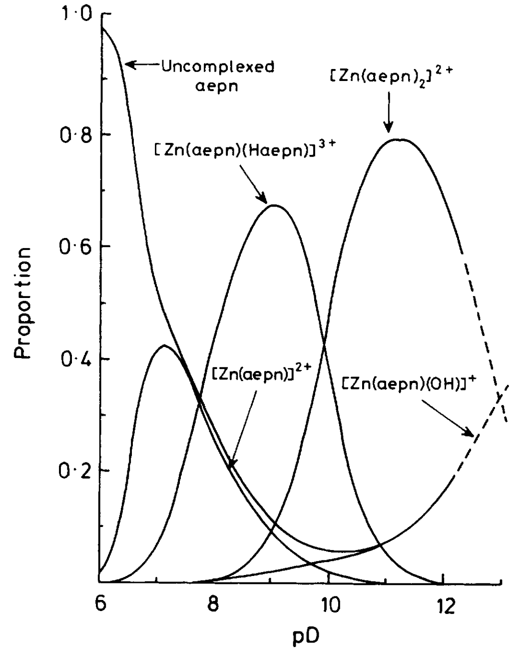


Figure 5. Distribution diagram for the various complexes and uncomplexed aepn in Zn + aepn solutions (0.20 + 0.40 mol dm^{-3})

chemistry[21] in very alkaline solution (and this uncertainty above pD *ca.* 12.1 is reflected in the use of broken lines in Figure 5); the direction of movement of the C_b and C_c lines does, however, confirm the 'crossing' assignment made for these carbons in the free-ligand profile. Secondly, the differential line broadening in the pD range 6—9 can be explained by the difference in δ for the free and complexed ligand. Thus, at pD 6.95 and concentrations of aepn and Zn of 0.58 and 0.20 mol dm^{-3}, respectively, the relative linewidths are $C_e > C_c > C_b,C_d > C_a$ and the corresponding values of $|\delta_{free} - \delta_{complexed}|$ are 4.3, 3.2, 2.4, 2.3, and 1.3 p.p.m. Thirdly, a 'crossover' between C_b and C_c at around pD 9 in the 0.58 + 0.20 mol dm^{-3} system (not shown) could be demonstrated experimentally. Finally, it is not possible to obtain the high level of agreement between calculated and observed shifts seen in Figure 3 (and also for the 0.58:0.20 molar ratio) using any other combination of peak assignments.

Initial attempts to compute the two sets of experimental data assuming the formation of only the published[6] species, namely [ML], $[ML_2]$, and [ML(OH)], were unsuccessful, especially in the pD range 8—10. In view of the requirement for a protonated bis species [ML(HL)] in the trien[3] and dien[5] systems, such a species was added for the aepn system also, where it was found to rationalise the discrepancies well. (The failure of Barbucci *et al.*[6] to find evidence for such a species is understandable since, under their conditions [initial concentration of aepn = 0.90 × 10^{-2} and Zn = 0.80 × 10^{-2} mol dm^{-3}], we calculate that the fraction of aepn present in the bis complexed forms would not exceed 0.09.) The computed 'best fit' curves, obtained using the chemical shifts and equilibrium constants listed in Tables 1 and 3, are shown as solid lines in Figure 3. Confirmation of the formation of [ML(HL)] was obtained through the potentiometric titration of a solution of zinc + aepn under comparable conditions (0.088 + 0.176 mol dm^{-3} in D_2O). As with the dien system,[5] the quality of fit was not significantly altered by whether or not the protonated monocomplex $[Zn(Haepn)]^{3+}$ was included in the analysis. In view of this and of the tendency for $Zn(OH)_2$ to precipitate from decimolar solutions with a lower aepn:Zn ratio than 2:1 (which therefore precludes the use of more favourable conditions) the formation of this species could not be confirmed. As with the dien system, [M(HL)] has not been included in the analysis of the n.m.r. data.

3. *The Ternary Systems.*—The measured chemical shifts of the C atoms of the ligands in the following mixtures at different pD are given in the supplementary material (SUP 56716): Zn (0.10 mol dm^{-3}) + dpt (0.20 mol dm^{-3}) + en, pn, or gly (0.10 mol dm^{-3}); Zn (0.20 mol dm^{-3}) + aepn (0.40 mol dm^{-3}) + en, gly, ala, or β-ala (0.20 mol dm^{-3}); Zn (0.10 mol dm^{-3}) + aepn (0.15 mol dm^{-3}) + pn (0.10 mol dm^{-3}); Zn (0.10 mol dm^{-3}) + aepn (0.20 mol dm^{-3}) + dach (0.10 mol dm^{-3}). In all cases, the X

Table 3. 'Best'[a] ^{13}C chemical shifts[b] (in p.p.m.) and formation constants[c] for zinc–aepn complexes

		δ(aepn)							
Complex		C_a	C_b	C_c	C_d	C_e		δ(X)	log K^{ML}_{MLX}
$[Zn(aepn)]^{2+}$	[ML]	39.35	48.70	49.67	28.30	42.60			8.77[d]
$[Zn(aepn)(Haepn)]^{3+}$	[ML(HL)]	39.50	48.00	48.23	27.32	41.40			2.95[e]
$[Zn(aepn)_2]^{2+}$	$[ML_2]$	40.05	49.95	51.15	29.60	43.20			3.85
$[Zn(aepn)(OH)]^+$	[ML(OH)]	39.40	48.70	51.10	27.60	43.60			9.63[f]
$[Zn(aepn)(en)]^{2+}$	[MLA]	38.90	47.85	50.00	27.00	44.10		40.75	4.62
$[Zn(aepn)(pn)]^{2+}$	[MLA]	39.20	48.90	49.80	28.00	43.60	C_a	44.00	3.30
							C_b	29.35	
$[Zn(aepn)(dach)]^{2+}$	[MLA]	39.10	48.10	50.20	27.60	44.20	C_a	55.85	5.48
							C_b	35.70	
							C_c	25.85	
$[Zn(aepn)(glyO)]^+$	[MLA]	39.10	47.70	50.10	26.85	43.90	CH_2	43.27	4.13
$[Zn(aepn)(alaO)]^+$	[MLA]	39.10	47.40	49.85	26.40	44.00	C_a	20.75	3.74
							C_b	50.73	
							CO_2^-	183.70	
$[Zn(aepn)(\beta\text{-alaO})]^+$	[MLA]	39.50	48.35	51.00	27.25	43.90	C_a	38.85	2.90
							C_b	36.30	
							CO_2^-	181.75	
$[Zn(aepn)(ala)]^{2+}$	[ML(HA)][g]	*h*	*h*	*h*	*h*	*h*	C_a	19.95	1.00
							C_b	50.57	
							CO_2^-	183.00	

[a] The 'best' values for the binary system were determined from 18 (Zn + aepn, 0.20 + 0.40 mol dm^{-3}) and 6 (Zn + aepn, 0.20 + 0.58 mol dm^{-3}) sets of data points, respectively, with standard deviations of 0.055, 0.040 (C_a); 0.093, 0.100 (C_b); 0.060, 0.082 (C_c); 0.080, 0.052 (C_d); 0.116, 0.027 p.p.m. (C_e). For the ternary systems, the numbers of data points (in parentheses) and standard deviations (in p.p.m.) for X and L (C_a, C_b, C_c, C_d, C_e) were, respectively: en (14), 0.042, 0.067, 0.103, 0.096, 0.075, 0.059; pn (10), 0.039 (C_a), 0.036 (C_b), 0.128, 0.087, 0.093, 0.087, 0.094; dach (6), 0.024 (C_a), 0.047 (C_b), 0.084 (C_c), 0.077, 0.094, 0.034, 0.040, 0.025; gly (12), 0.031 (CH_2), 0.070, 0.104, 0.094, 0.076, 0.041; ala (12 for C_a, C_b; 8 for CO_2^-), 0.062 (C_a), 0.058 (C_b), 0.081 (CO_2^-), 0.038, 0.071, 0.048, 0.033, 0.190; β-ala (8), 0.069 (C_a), 0.060 (C_b), 0.100 (C_c), 0.063, 0.069, 0.031, 0.068, 0.072. [b] The estimated values are ±0.3 p.p.m. for [ML(OH)], otherwise ±0.1 p.p.m. [c] Temperature 21 ± 1 °C; *I* various. $K^{ML}_{MLX} = [Zn(aepn)X]/[Zn(aepn)][X]$ with X = $Haepn^+$, aepn, en, pn, dach, glyO, alaO, β-alaO, or ala. The estimated errors in log K^{ML}_{MLX} are ±0.1 for [MLA] and ±0.2 for $[ML_2]$ and [ML(ala)]. [d] Assumed value for stability constant of $[Zn(aepn)]^{2+}$ (from ref. 6). [e] Equivalent to a $pK_D{}^c$ value for [ML(HL)] of 9.85. [f] $pK_D{}^c$ value for [ML]; estimated error is ±0.2. [g] Formulation uncertain. [h] Reliable value unobtainable.

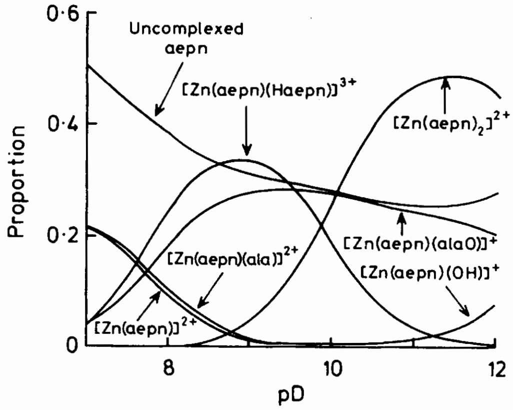


Figure 6. Distribution diagram for the various complexes and uncomplexed aepn in Zn + aepn + ala (0.20 + 0.40 + 0.20 mol dm^{-3})

resonances were consistently sharp and of the expected intensity, indicating rapid exchange. Representative plots of the pD profiles for the X ligand are shown in Figure 2. The solid lines were computed using the formation constants K^{ML}_{MLX} and chemical shifts δ(X) listed in Tables 2 and 3, and assuming the computed pD profiles of the free ligand (*cf.* broken lines in Figure 2). In the cases of Zn + dpt + pn, Zn + dpt + gly, and Zn + aepn + ala it was necessary to incorporate parameters for a monoprotonated ternary complex in addition to those for the expected ternary complex [MLA], as illustrated in Figure 2 (*a*)—(*c*) where the dotted lines have been constructed assuming that only [MLA] is formed. In the other systems, the data for X could be fitted satisfactorily without involving a protonated ternary species [*cf.* Figure 2(*d*) and (*e*)].

The chemical-shift profiles for the C atoms of aepn and dpt in the ternary systems are not shown as they are similar to those for Zn + dpt (Figure 1) and Zn + aepn (Figure 3). The spectral lines for aepn and C_b of dpt were similar in appearance to those in the corresponding binary system while those for C_a and C_c of dpt were somewhat sharper; hence fast exchange was assumed throughout the pD ranges studied. A representative distribution diagram (for Zn + aepn + ala) is shown in Figure 6.

Discussion

The results given in Tables 2 and 3 show close similarities between the co-ordination chemistries of zinc with the triamines aepn and dpt. In addition to the aqua form of the mono complex [ML], there is evidence in each case for the formation of a hydroxo–mono complex [ML(OH)], and for both an unprotonated and a monoprotonated form of the bis complex, $[ML_2]$ and [ML(HL)]. Although [ML(OH)] and $[ML_2]$ have been reported previously[6–8] for both ligands, $[Zn(aepn)_2]^{2+}$ is the only one of the four complexes on the formation of which two literature reports[6,7] agree. For neither ligand has the complex [ML(HL)] been reported previously and it seems likely that its omission from the analysis (coupled with the less than ideal concentration and pH ranges used for the titrations) is the main reason for the confusion in the literature on these systems. Ternary complexes [MLA] are formed with a range of potentially bidentate ligands A but in only a few cases was evidence found for the formation of a monoprotonated form, though it cannot be ruled out elsewhere. In no case was there evidence for a doubly protonated ternary form $[M(HL)_2A]$, of the type observed with dien.[5] The implications of the present results as to the co-ordination geometries adopted by zinc in its aepn and dpt complexes will be discussed below, but first we shall consider the ^{13}C chemical shifts themselves and the extent to which they conform to the patterns found with other systems.

The effect, on the resonance of a carbon in a linear polyamine, of protonating a neighbouring amino group is invariably to move it upfield.[12,22] To a first approximation the effect, on the same carbon, of forming a zinc chelate is[3,5,9–11] equivalent to half protonating it if it becomes part of a five-membered ring, but if it becomes part of a six-membered ring the effect depends on the position of the CH_2 group along the chain: if it is β to the N atoms it behaves as if it were in a five-membered ring, but if it is α, γ to the N atoms the resonance moves several p.p.m. downfield. Although for most carbon atoms there is a little more variation within the dpt and aepn series than has been found previously (which is partly attributable to the larger uncertainties in the computed aepn and dpt δ values), the same general pattern is observed. If the values for the bis complexes are omitted (see below), the average δ values for C_a and C_b in the aepn complexes are 39.21 ± 0.18 and 48.21 ± 0.50 p.p.m., which are about half way between 41.00 and 52.10 p.p.m. for the unprotonated form of the free ligand, and 36.55 and 45.45 p.p.m. for its fully protonated form. Similarly, the average for C_b in the dpt complexes is 27.93 ± 0.39 p.p.m. compared with 32.90 and 24.77 p.p.m. for the free ligand, and for C_d in aepn the corresponding figures are 27.38 ± 0.58, 32.75, and 24.75 p.p.m.

On the other hand, the average δ values for the α,γ-carbons in the complexes are all some 3—4 p.p.m. higher than in the unprotonated ligand: for dpt $\delta(C_a)$ and $\delta(C_c)$ are 43.98 ± 0.29 and 51.30 ± 0.25 p.p.m. in the complexes and 39.85 and 47.42 p.p.m. in L, while for aepn $\delta(C_c)$ and $\delta(C_e)$ are 50.22 ± 0.51 and 43.74 ± 0.47, and 47.30 and 39.80 p.p.m., respectively. The diagnostic value of this singular downfield shift of the α,γ-carbon resonances in six-membered zinc chelate rings has already been noted[11] and it was primarily to obtain additional evidence on its origin that the zinc–aepn ternary complexes of dach and β-ala were studied. Our previous results had indicated that, contrary to the position[23] with cobalt(III) and presumably[24] other diamagnetic metal ions with partially filled *nd* sub-shells ($n \geq 3$), inductive effects are not transmitted from one part of the zinc complex to another, through the metal ion. This suggested that the α,γ downfield shift was steric rather than inductive in origin and that similar behaviour might be found in derivatives of cyclohexane and in other six-membered ring systems.

There is an extensive literature[25] on the effect of a substituent Z on the chemical shift of a carbon atom in an aliphatic compound. The α effect is mainly inductive in origin and its size and direction are a measure of the electronegativity of Z (δ increasing as electronegativity increases). The C atom(s) in the β position experience(s) the intramolecular field of the substituent (which is related to its steric disposition) as well as its inductive effect but, since most of these fields cannot be described quantitatively, there is no simple correlation between the β effect and the chemical nature of Z. The γ effect, if there is one, is almost entirely steric in origin and usually involves a decrease in δ. In acyclic compounds, rapid rotation about the C–C bonds means that all substituent effects are averaged over many possible rotamers but in structures based on cyclohexane there is less molecular flexibility and this must be borne in mind when assessing the effects of substitution here and in similar ring systems.[26–28] In the case of dach, the effect of complex formation on the δ values of all three ring carbons (Tables 1 and 3) can be understood in terms of the established behaviour of substituted cyclohexanes.

In saturated six-membered carbocyclic rings the chair conformation is so favoured energetically over the boat form that the latter can generally be disregarded.[29] *trans*-1,2-Disubstituted cyclohexanes can exist in two chair forms, the a,a conformer in which the substituents are both in the axial position and the e,e conformer in which they are both equatorial. In the case of *trans*-1,2-dimethylcyclohexane an equilibrium is established between the readily interconvertible diaxial and diequatorial forms which greatly favours the latter. However, where the substituents are polar (as in the dibromo and dicarboxylate analogues) the diaxial form makes an appreciable contribution because the diequatorial form, though favoured sterically, is destabilised by dipolar repulsion.[29] A similar result would be expected for dach. On the other hand, the conformation of dach in its zinc complexes must be diequatorial if, as the relatively high stability constants (*cf.* Table 2 and ref. 18) for $[Zn(aepn)(dach)]^{2+}$, $[Zn(dach)]^{2+}$, and $[Zn(dach)_2]^{2+}$ suggest, the chair form is retained. This implies that a significant proportion of the dach changes its conformation from a,a to e,e when a zinc complex is formed. Breitmaier and Bauer[28] have listed parameters from which it is possible to estimate the chemical shifts of the C atoms in axially and/or equatorially substituted cyclohexanes. Using interpolated values of $z_\alpha = 25$, $z_\beta = 7$, $z_\gamma = -6$, and $z_\delta = 0$ for the axial-amino parameters, we calculate that the changes in chemical shift which would be experienced by the carbon atoms in dach if 50% were to undergo this a,a→e,e transition would be +1.0 for C_a, +3.1 for C_b, and +1.5 p.p.m. for C_c. (Substitution parameters are not available for the $-NH_3^+$ group.) These compare well with the actual changes in δ which accompany complex formation, namely +0.5, +3.5, and +0.9 p.p.m., and provide further support for the proposition that the effects of zinc complex formation on ^{13}C chemical shifts are to be understood simply in terms of the imposition of certain steric constraints on the various parts of the ligand(s) and the effective partial protonation of its co-ordinating atoms (though the effect of the latter would seem to be quite small in the case of dach).

Let us now turn to the six-membered rings of the zinc–dpt and zinc–aepn complexes and consider how well they can be described in terms of established behaviour. Eliel and Pietrusiewicz[30] have reviewed the effects of the substitution of one or more heteroatoms on ^{13}C chemical shifts in non-aromatic ring systems and good models for the β-carbon (*i.e.* C_b in dpt and C_d in aepn) would seem to be C^5 in the 1,3-disubstituted and C^4 in the monosubstituted cyclohexanes which often have δ values close to that of cyclohexane itself (27.7 p.p.m.). For example, $\delta(C^5)$ in 1,3-dioxane, 1,3-dithiane, and 1,3-oxathiane are 26.8, 26.6, and 27.0 p.p.m. while $\delta(C^4)$ in piperidine, tetrahydropyran, and thiane are 27.5, 26.9, and 28.2 p.p.m. (Unfortunately the diaza analogue, hexahydropyrimidine, is unstable and its ^{13}C spectrum does not appear to have been reported.) Similar values are observed for most of the dpt (δ 27.9) and aepn (δ 27.4) complexes studied here.

With the α,γ carbons (C_a, C_c in dpt and C_c, C_e in aepn) it is difficult to decide *a priori* how much of the observed zinc-complexation shift is attributable to changes occurring at the α nitrogen (which will presumably be largely inductive in nature) and how much is due to the presence of the γ nitrogen, which should be largely of steric origin. Although the effect on a carbon of a single α-heteroatom substitution in cyclohexane is,[30,31] as expected, strongly dependent on the electronegativity, there has been no systematic investigation of the effect of 1,3-diheteroatom substitution. On the assumption that the α effect will be similar to that observed in a single-atom substitution, we conclude that the partial transfer of the lone pair to the zinc atom will produce an upfield α shift, as it does on protonation.

This implies that the closure of the ring itself is responsible for changing the steric interactions and thereby producing a downfield shift of some 3.5—4.5 p.p.m. at the γ carbons. This ring-closure effect does not appear to have been reported previously, although we have noted its occurrence[11] in six-membered rings containing oxygen and silicon. It is also found on passing from 1,3-propanediol (δ 59.2)[25] to 1,3-dioxane (δ 65.9)[28] but not on forming glutaric anhydride from its acid (δ 33.2$\rightarrow$30.0)[32] or on going from n-heptane to cyclohexane (δ 32.4$\rightarrow$27.7);[25] neither is it observed on forming the β-alaninate(1 $-$) complex of $[Zn(aepn)]^{2+}$ (Tables 1 and 3). These observations indicate a requirement for at least one H-atom on each α,γ-carbon in addition to the heteroatoms in the 1,3-positions, but not for the zinc atom in the 2 position. Our general conclusion, therefore, is that the chemical shifts of all three carbons in these $\overline{N(CH_2)_3NZn}$ rings are similar to those found in other heterosubstituted cyclohexanes.

The only zinc complex of either aepn or dpt whose structure has been determined is that of $[\{Zn(dpt)\}_2(\mu\text{-ox})][ClO_4]_2$ (ox = oxalate) in which the co-ordination geometry is best described[33] as trigonal bipyramidal. The secondary nitrogen occupies one of the axial and the primary nitrogens two of the equatorial positions, while the other axial and equatorial positions are taken by two of the oxalate oxygens. (Some of the dimensions are actually rather distorted at one of the zinc centres owing to the need to accommodate one of the perchlorate ions.) Interestingly, this is a similar arrangement to that found[34] in the only 1 : 1 zinc–dien complex whose structure is known, $[Zn(dien)(bipyam)]^{2+}$ (bipyam = di-2-pyridylamine), but it differs from that usually found in dpt complexes where the disposition of the nitrogens is meridional. That this more common arrangement is possible for a metal the size of Zn^{2+} ($r_+ = 0.74$ Å) is indicated by its adoption in $[Ni(dpt)_2][ClO_4]_2$ (ref. 35; $r_+ = 0.69$ Å), and there is evidence that the trigonal-bipyramidal geometry is favoured by Zn^{2+} (with its greater co-ordinational flexibility than Ni^{2+}) because it involves less intramolecular repulsion near the secondary nitrogen. At the undistorted zinc centre of $[\{Zn(dpt)\}_2(ox)]^{2+}$ the chelate rings both have[33] the chair conformation and are disposed, back-to-back, so that an approximate mirror relation exists across a plane through their common Zn–N (secondary) bond. In the complexes containing meridionally disposed dpt, on the other hand, the presence of the chair-distorted boat conformation[36,37] or a significant lengthening of the metal–ligand bonds {as in $[Ni(dpt)_2]^{2+}$, ref. 35} suggests considerable intramolecular strain, and this has been confirmed[38] through force-field calculations. A similar relationship appears to exist[5] in the zinc–dien complexes between the trigonal-bipyramidal Zn(dien) moiety (strain-free) and the *mer*-octahedral $[Zn(dien)_2]^{2+}$ ion, in which the lengthening of the Zn–N (primary) bonds indicates intramolecular strain. Although structural and force-field minimisation data are lacking for aepn complexes, the thermodynamic and ^{13}C n.m.r. data reported here suggest a single structural pattern for all three systems.

The lack of a simple relationship between formation constant and ligand denticity for zinc complexes has already been emphasised;[9,11] nonetheless, the equilibrium constants for dpt, aepn (Tables 2 and 3) and dien (ref. 5) do, on the whole, behave regularly. The stabilities of the $[ML_2]$ complexes follow the order already established for ML, dien > aepn > dpt [log K_1 = 9.00, 8.77, 7.92; log K_2 = 4.30, 3.85, 2.48], consistent with the generalisation that a five-membered chelate ring is more stable than a six-membered one.[2] The fact that the dien $-$ aepn increments are smaller than those for aepn $-$ dpt suggests that there is a slight preference for the mixed 5/6-ring arrangement of aepn, which is much more pronounced[39] in the tetramine complexes of strongly directional metal ions such as nickel(II). The pK_D^c values for $[ML_2]$ (8.70, 9.85, 11.00) follow the same order, dien < aepn < dpt, as those of the ligands themselves (10.30, 10.75, 11.20) and in each case the value for aepn is the average of those for the other two. The ternary stability constants for en and pn follow the order dien $\simeq$ aepn > dpt (dien $\simeq$ aepn for alaO), while the dien value is depressed for glyO {as is the dien formation constant for [ML(HL)] from [ML] + HL}; the incremental difference (aepn $-$ dpt) for log K^{ML}_{MLA} is about 1.1 in each case. For alaO and β-alaO, the difference in their ternary stability constants with $[Zn(aepn)]^{2+}$ is about the same as the differences in the formation constants of both their 1 : 1 and 1 : 2 complexes with zinc (Δlog *K ca.* 0.8, 0.8, and 1.0, respectively).

The general consistency of the ^{13}C chemical shifts for aepn and dpt systems with those found for other zinc complexes has been noted; to what extent do the values for the individual complexes suggest structural conclusions?

In the first place, the δ values for en, pn, and glyO in [MLA] indicate[11] that these ligands all bind in a bidentate fashion and there is no reason to think otherwise for other A. Moreover, for both L ligands, the corresponding chemical shifts of [ML], [ML(OH)], and [MLA] are so similar as to suggest that the disposition of the L moiety within each set is the same. In both cases L is terdentate and the most reasonable conclusion is that here, as with the dien analogues,[5] the trigonal-bipyramidal arrangement is retained. {Although there is no direct structural information on aepn complexes and so the possibility of octahedral co-ordination in the mono complexes cannot be ruled out, the differences in chemical shift compared with $[Zn(aepn)_2]^{2+}$ argue against the *mer* configuration while molecular models suggest that the *fac* configuration would be very strained.}

As for the bis complexes, full co-ordination is indicated in $[Zn(aepn)_2]^{2+}$ by the fact that $\delta(C_c)$ and $\delta(C_e)$ are similar to the values for the aepn mono complexes. The small increases in $\delta(C_a)$ and $\delta(C_b)$ are unlikely to be associated with ring opening since the five-membered ring would be expected[2] to be more stable than the six-membered one. In keeping with this, the δ values for $[Zn(aepn)(Haepn)]^{3+}$ indicate that the proton is located on the primary amino group next to C_e rather than on that next to C_a. A more likely origin of the downfield shifts of C_a and C_b resonances in $[Zn(aepn)_2]^{2+}$ is the inter-ring strain mentioned above, to which a similar movement of the C_b resonance of $[Zn(dien)_2]^{2+}$ has been attributed.[5] The same reason can be adduced for the high $\delta(C_d)$ in $[Zn(aepn)_2]^{2+}$ and $\delta(C_b)$ in $[Zn(dpt)_2]^{2+}$, and the comparatively low values of $\delta(C_a)$ and $\delta(C_c)$ in the latter complex. An alternative rationalisation for the movement of all three resonances in $[Zn(dpt)_2]^{2+}$ compared with the mono complexes, in which each dpt has become bidentate, cannot be ruled out but it would imply that each dpt in $[Zn(dpt)(Hdpt)]^{3+}$ is also bidentate since it is unreasonable to propose a *reduction* in ligand denticity to accompany the deprotonation of [ML(HL)]; presumably the two unco-ordinated amino groups would be joined through hydrogen bonding since there would otherwise be no obvious reason for the C_a, C_c line broadening observed with Zn + dpt throughout the accessible pH range. The chemical shift differences between $[Zn(dpt)(Hdpt)]^{3+}$ and the dpt mono-complexes can also be interpreted in these terms but they are equally consistent with five-co-ordination and we favour this simpler interpretation since it is also suggested by the δ values of $[Zn(aepn)(Haepn)]^{3+}$.

In summary, the available data are all consistent with a common structural pattern for the zinc complexes of the linear triamines dien, aepn, and dpt in solution: where any additional ligands present (including H_2O) are monodentate or bidentate, the trigonal-bipyramidal arrangement is adopted, with the secondary nitrogen in the axial position; but where an extra ligand is a second molecule of the triamine (or presumably any other suitable tridentate ligand) the co-ordination number of the metal rises to six and a *mer*-octahedral configuration results.

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