Complexes formed between Zinc(II) and Diethylenetriamine: A Carbon-13 Nuclear Magnetic Resonance Study†

David N. Hague* and Anthony D. Moreton
University Chemical Laboratory, Canterbury, Kent CT2 7NH

Carbon-13 n.m.r. spectra are reported as a function of pH for mixtures of diethylenetriamine (dien) and zinc nitrate, and of zinc and dien with 1,2-diaminoethane (en), 1,3-diaminopropane (pn), acetate, glycine (gly), and L-alanine (ala). Carbon-13-chemical shifts are also reported as a function of pH for dien and gly (carboxylate carbon) alone. The pH profiles have been analysed by computer and the chemical shifts of the methyl, methylene, methine, and carboxylate carbon atoms determined for the following species: dien, Hdien$^+$, H_2dien^{2+}, H_3dien^{3+}, [Zn(dien)]$^{2+}$, [Zn(dien)(Hdien)]$^{3+}$, [Zn(dien)$_2$]$^{2+}$, [Zn(dien)(en)]$^{2+}$, [Zn(dien)(pn)]$^{2+}$, [Zn(dien)(MeCO$_2$)]$^+$, [Zn(dien)(glyO)]$^+$, [Zn(dien)(alaO)]$^+$, [Zn(Hdien)$_2$(en)]$^{4+}$, [Zn(Hdien)$_2$(pn)]$^{4+}$, [Zn(Hdien)$_2$(glyO)]$^{3+}$, [Zn(Hdien)$_2$(alaO)]$^{3+}$. Stability constants have also been determined for the bis and ternary complexes. [Zn(dien)(OH)]$^+$ does not appear to be formed to any significant extent. Potentiometric titrations with dien and zinc + dien solutions provide support for the interpretation of the chemical-shift data. The implications of the results as to the co-ordination geometry of zinc in these complexes are discussed.

In the course of an investigation into the possible use of ^{13}C n.m.r. spectroscopy to determine the co-ordination geometry of zinc complexes with organic ligands, we have shown[1–3] that it is possible to identify individual complexes in rapidly exchanging equilibrium mixtures through the chemical shifts of their non-equivalent carbon atoms. By means of a least-squares computer analysis of the pH profiles for the ligands in the absence and presence of zinc we were able to determine the chemical shifts for the major species present and the relevant pK_a values and stability constants.

The first purpose of the present paper is to report the use of the technique to identify and characterise the major zinc complexes present in aqueous solutions containing 3-azapentane-1,5-diamine (diethylenetriamine, dien), since the current literature[4–7] on this system is conflicting. Although there is general agreement about the stability constant of the principal 1:1 complex [Zn(dien)]$^{2+}$ ($\log K_f \simeq 9$), there is no consensus about even the identity of any other complex which might be formed. Jonassen *et al.*[5] and McIntyre *et al.*[6] make no mention of one, but Prue and Schwarzenbach[4] and Arishima *et al.*[7] both characterised the 2:1 complex [Zn(dien)$_2$]$^{2+}$ ($\log K_2 = 5.5$ and 4.9, respectively) and agree that at least one other complex is formed. However, they disagree over its identity: Prue and Schwarzenbach favour a hydroxy complex [Zn(dien)(OH)]$^+$ by analogy with the well characterised copper(II) species but do not determine its stability constant, while Arishima *et al.* prefer the protonated form [Zn(Hdien)]$^{3+}$ and report a (log) stability constant for it of 4.1. We now provide ^{13}C n.m.r. data (and supporting potentiometric evidence) which confirm the formation of the bis complex [Zn(dien)$_2$]$^{2+}$ and argue that the hydroxy complex is not a significant form, at least below pH 12. Although it is not possible to draw a firm conclusion about the formation of [Zn(Hdien)]$^{3+}$, our data do indicate that the previously unreported protonated bis complex [Zn(dien)(Hdien)]$^{3+}$ is important around pH 8.

The second purpose of this paper is to report the application of the ^{13}C n.m.r. technique to characterise the ternary complexes formed in solutions containing zinc, dien, and a series of mono- or bi-dentate ligands, X. In our studies with triethylenetetramine (trien)[1,2] and 2,2′,2″-triaminotriethylamine (tren),[3] we found that the identities of the analogous ternary complexes formed and the values of their chemical shifts provided evidence about the co-ordination number(s) of zinc when bound to these ligands, and in the following paper[8] we report the use of the same method to investigate the complexes with another tetramine, 3,7-diazanonane-1,9-diamine (dadn). In the dien system, which provides an interesting contrast to these tetramine systems, the simple ternary complex [Zn(dien)A]$^{n+}$ ($n = 1$ or 2) is formed in each case (A = glyO, alaO, en, pn, or MeCO$_2^-$) while with the bidentate ligands the major ternary species formed in the weakly alkaline pH range (*ca.* 7—9) is [Zn(Hdien)$_2$A]$^{m+}$ ($m = 3$ or 4). Bis(protonated dien) ternary complexes have not been reported before. The results are discussed with a view to establishing the co-ordinational preference of zinc when bound to dien.

Experimental

Procedures.—The solutions were made up as described previously,[9,10] those for the ^{13}C n.m.r. experiments being in D_2O; pD = pH meter reading + 0.40. The n.m.r. spectra were recorded[1,9] at 21 ± 1 °C with a JEOL FT-100 or Bruker WM-200/WB instrument, and the potentiometric titrations (in H_2O) performed[10] under a CO_2-free atmosphere using initial volumes of 5.50 cm^3 and [NaOH] = 1.00 mol dm^{-3}. Temperature control was achieved in the n.m.r. experiments through air-conditioning and the use of compressed air. Chemical shifts are estimated to be reliable to ±0.04 p.p.m.; they were measured relative to internal 1,4-dioxane (δ 67.71) and are quoted on the δ scale.

Analysis.—Although the methods used for the analysis of the ^{13}C n.m.r. and potentiometric data have already been outlined,[10] it will be helpful for the discussion of our present

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† *Supplementary data available* (No. SUP 56688, 8 pp.): observed chemical shifts for solutions containing dien. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1987, Issue 1, pp. xvii—xx.

The notation used throughout this paper is as follows: gly = glycine, glyO = glycinate(1−), ala = L-alanine, alaO = L-alaninate(1−), en = 1,2-diaminoethane, pn = 1,3-diaminopropane; ligand X = A (glyO, alaO, en, pn, or MeCO$_2^-$) or HA (gly, ala, Hen$^+$, or Hpn$^+$); ligand L = dien.

results to highlight a few salient features here; both approaches are based on standard techniques (*cf.* refs. 11 and 12).

^{13}C *N.m.r. titrations.* The spectral lines for dien and X were consistently sharp and of approximately the relative intensities predicted from the molar concentrations of the respective non-equivalent C atoms, bearing in mind the number of neighbouring H atoms. Our analysis has therefore assumed rapid exchange between the various complexed and uncomplexed forms of the ligands.

The observed chemical shift, δ, for a particular C atom is the average of the chemical shifts of that carbon in the various species present (δ_i), weighted according to their fractional populations (p_i): $\delta = \Sigma p_i \delta_i$. Thus for free dien, which can exist in the un-, mono-, di-, and tri-protonated forms (L, HL, H_2L, and H_3L, respectively), the chemical shift at a particular pH is given by equation (1). (For simplicity, the charges on ions are

$$\delta = p_L\delta_L + p_{HL}\delta_{HL} + p_{H_2L}\delta_{H_2L} + p_{H_3L}\delta_{H_3L} \qquad (1)$$

generally omitted and the predominantly deuteriated forms are referred to as protonated and represented by HL, H_2L, *etc.*) The fractional populations are also related through the three acid dissociation constants of dien and the procedure for fitting the computer-generated titration curves to the experimental points involved finding the set of parameters (seven for each curve in this case: δ_i for C_a and C_b in each of the four forms of dien, and the three pK_a values) which produced the smallest total variance in terms of the observed δ. Initial values were obtained by inspection and it was assumed that the pK_a values are the same for C_a and C_b.

Addition of a comparable concentration of zinc to a dien solution at pH > 5 generally results in a change in the chemical shifts owing to the conversion of some free dien into one or more complexed form. The chemical shift at a particular pH is now given by equation (2), where the first term on the right is

$$\delta' = \Sigma p_u\delta_u + \Sigma p_c\delta_c \qquad (2)$$

a composite one containing all the contributions from the uncomplexed ligand [and is some multiple of equation (1)] and the second one represents the contributions from the various complexes. The computer program calculated δ' according to equation (2) using the curve already generated for the free ligand and assumed chemical shifts and stability constants for the various complexes, and again the total variance between calculated and measured chemical shifts was minimised. As before,[1-3] the standard deviations for the various C atoms calculated from the differences between the observed δ or δ' and those computed on the basis of the parameters listed have been used as a guide to the quality of fit of the pD profiles. In view of the composite nature of δ and δ', it is not possible to give more than an estimate of the reliability of the individual chemical shifts.

Potentiometric titrations. Since the purpose of these titrations was to obtain supporting evidence for our interpretation of the n.m.r. data, comparable concentrations (decimolar) were employed to those used in the n.m.r. experiments. These are higher than is common in potentiometry and their use made it impracticable to try to maintain a constant background ionic strength. Moreover, the high insolubility of $Zn(OH)_2$ made it necessary to have a considerable excess of dien present above *ca.* pH 7. We performed two sets of titrations, one involving free dien and the other a 2:1 dien–zinc mixture, and performed a least-squares fit of the experimental points with computer-generated titration curves. The procedure involved[10] solving, at regular pH intervals, a polynomial generated by expressing the concentrations of all the dien-containing species in terms of the concentration of unprotonated free dien (L), assuming values for the various equilibrium constants. Allowance was made for the dilution accompanying each addition of NaOH but not the varying ionic strength (see below).

In the n.m.r. titrations, the calculated chemical shift for a particular experimental point is determined essentially by the chemical shifts of (and equilibrium constants involving) only those species which are dominant at the pH in question. This means that the reliability of the determined parameters depends on the extent to which the individual contributions can be made to stand out from the rest but not in any systematic way on the distant points in the titration curve. With the potentiometric titrations this is not so: any small error in computed volume added at the beginning of the curve will increase in significance as the titration proceeds. So as to minimise this effect in the pH region of prime concern (8—12), we started our potentiometric titrations at pH 6.5 rather than near pH 4 where 1:1 complexes are first formed.

Results

1. *The Free Ligands.*—The non-equivalent C atoms in dien, alaO, and pn are identified as follows: $NH_2C_aH_2C_bH_2$-$NHCH_2CH_2NH_2$, $C_aH_3C_bH(NH_2)CO_2^-$, and $NH_2C_aH_2C_b$-$H_2CH_2NH_2$ respectively. The measured chemical shifts, δ, for C_a and C_b in dien at different pD are represented by triangles in Figure 1. The titration curves (dashed lines) were computed from these data using the pK_a values (p$K_D{}^c$) and chemical shifts listed in Table 1. The agreement between our values of δ for dien (41.00 and 51.78) and those of Casy[13] (41.18 and 51.90) is good. The data for the potentiometric titration of dien (triangles) together with the computed curve (dashed line) are shown in Figure 2; the derived pK_a values (p$K_H{}^c$) are listed in Table 1. A previous investigation[10] with a homologous triamine, *N*-(2-aminoethyl)propane-1,3-diamine, had indicated that the protonated forms of the free ligand should be treated as hybrid rather than multiply charged ions when determining their contributions to the ionic strength. The closeness-of-fit for dien between the computed curve and the experimental points over the whole pH range studied supports this conclusion and justifies our not attempting to correct for ionic strength changes during the titration.

We have found six reported determinations[4,6,7,14-16] of the acid dissociation constants of H_3dien^{3+}, of which one[4] was performed under conditions similar to our own and another[14] generated data which can be extrapolated readily to our conditions. Our values of p$K_H{}^c$ (10.13, 9.39, and 5.00) agree well with the average of those of Prue and Schwarzenbach[4] and Jonassen *et al.*[14] (10.09, 9.37, and 4.79) but they are also rather closer than expected to the p$K_D{}^c$ values (10.30, 9.50, and 5.20), since the deuterium isotope effect ΔpK (= p$K_D{}^c$ − p$K_H{}^c$) is[10] typically around 0.6. However, quite large variations have been found[17] in ΔpK and it seems that dien has anomalously low values.

The triangles in Figure 3(*c*) represent the measured chemical shifts of the carboxylate C atom of free gly, which yielded chemical shifts in glyO and gly of 182.7 and 173.4 p.p.m., respectively. The broken lines in Figure 3 represent the computed pD profiles of free X (*cf.* refs. 2, 3, and 10). In the case of $MeCO_2^-$, we found no significant difference in carboxylate chemical shift (δ 182.5 ± 0.2) between deprotonated and complexed forms.

2. *The* Zn^{2+} + dien *System.*—The measured chemical shifts for zinc + dien (0.20 + 0.44 mol dm^{-3}) at different pD are represented by the solid circles in Figure 1. In fitting the computed curves, we started with the assumption that two complexes, $[Zn(dien)]^{2+}$ and $[Zn(dien)_2]^{2+}$ ([ML] and [ML_2]), are formed with respective (log) stability constants of *ca.* 9 and 5.

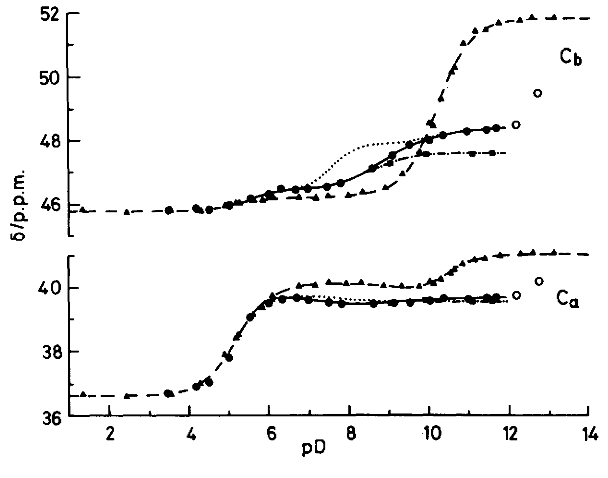

Figure 1. ^{13}C N.m.r. chemical shifts as a function of pD for dien (0.20 or 0.40 mol dm^{-3}, ▲) and zinc + dien (0.20 + 0.44 mol dm^{-3}, ●; or 0.10 + 0.15 mol dm^{-3}, ■)

Table 1. 'Best' ^{13}C chemical shift (in p.p.m.) and pK_a values for dien (L)

(*a*) Chemical shifts[a]

	δ(L)	δ(HL^+)	δ(H_2L^{2+})	δ(H_3L^{3+})
C_a	41.00	39.60	40.12	36.58
C_b	51.78	47.20	46.24	45.77

(*b*) pK_a

Measured (n.m.r.)[b]	$pK_D{}^c$	10.30	9.50	5.20
Measured (potentiometric)[c]	$pK_H{}^c$	10.13	9.39	5.00
Literature[d]	$pK_H{}^c$	10.09	9.37	4.79

[a] The estimated errors are ±0.1 p.p.m. for L, H_2L^{2+}, H_3L^{3+}, and ±0.2 p.p.m. for HL^+. The 'best' values were determined from 30 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 0.081 and C_b 0.059 p.p.m. [b] At 21 ± 1 °C; *I* various. The estimated errors (see also footnote *a*) are ±0.1 (first two values) and ±0.05 (third value). [c] At 20.0 ± 0.1 °C, $I \approx 0.4$ mol dm^{-3}; the estimated errors are ±0.1. Determined from 43 data points with a standard deviation of 0.006 cm^3 for the experimental volume of 1.00 mol dm^{-3} NaOH added from the values calculated on the basis of the parameters listed. [d] The average of data from ref. 4 (20 °C; $I = 0.5$ mol dm^{-3}) and ref. 14 (extrapolated to 20 °C; $I = 1.1$ mol dm^{-3}).

Besides the reports of Prue and Schwarzenbach[4] and Arishima *et al.*[7] to this effect, inspection of the experimental points for C_b reveals two plateau regions (at pD 6—8 and 10—12, respectively) where these could be the dominant forms. We found that it was not possible to obtain a combination of equilibrium constants and individual chemical shifts which would reproduce the experimental points on this basis alone since a combination which matched the plateau regions could not be made to fit the gentle curve linking them. This is illustrated in Figure 1, where the dotted lines were constructed on the basis of the parameters listed in Tables 1 and 2 for the species [ML], [ML_2], L, HL, H_2L, and H_3L only. If, however, the involvement of a protonated bis complex [Zn(dien)(Hdien)]$^{3+}$ {[ML(HL)]} is postulated in addition to the other species mentioned it is possible to fit the data well, as shown by the solid lines in Figure 1, [ML(HL)] and [ML_2] are linked by a $pK_D{}^c$ of 8.7.

A feature of the data which is not explained in terms of [ML], [ML_2], [ML(HL)], and uncomplexed dien is the trend towards the free ligand lines at pD > 12, represented by the open circles in Figure 1 and by additional points at pD > 13 which are not included because they fall outside the range of reliable pD measurements. It might be argued that this is caused by the formation of the hydroxy complex [Zn(dien)(OH)]$^+$ {[ML(OH)]} mentioned by Prue and Schwarzenbach[4] but this alone cannot be the explanation since it is impossible to deflect the computed curves through these points without destroying the fit at lower pD. (As explained below, it is also possible to exclude [ML(OH)] as the species responsible for the upper plateau region.) Although it is undoubtedly associated with the break-up of [$Zn(dien)_2$]$^{2+}$ to give hydroxy species and free dien, we have not tried to fit these data by computer in view of the likely[18] complexity of the situation.

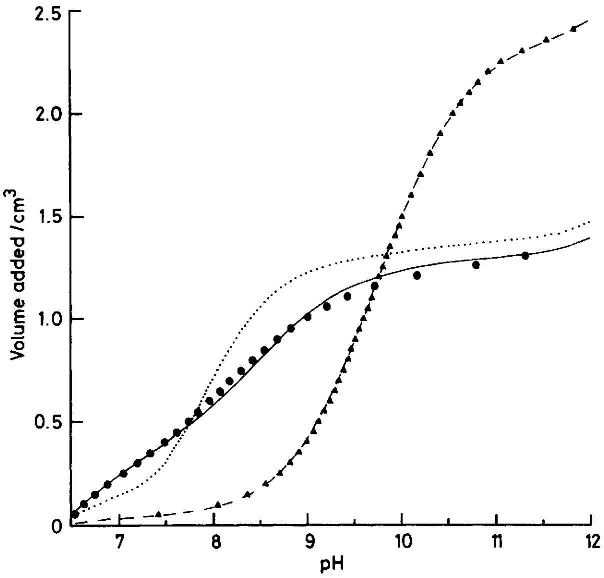

Figure 2. Potentiometric titration of dien (0.21 mol dm^{-3}, ▲) and zinc + dien (0.10 + 0.21 mol dm^{-3}, ●) in H_2O. NaOH (1.00 mol dm^{-3}) was added to 5.50 cm^3 of the solution

It is therefore possible to fit the chemical shift pD profiles for both C atoms in a zinc + dien solution (0.20 + 0.44 mol dm^{-3}) by a pair of curves computed on the basis of the formation of [ML], [ML_2], [ML(HL)], and the four uncomplexed forms of dien. Because of the large number of parameters involved in the computer simulation and the possibility that a spurious fit might occur through compensation between incorrect chemical shifts and equilibrium constants, we have obtained confirmatory evidence for our interpretation. This consists of (*i*) a partial ^{13}C chemical shift pD profile for a different zinc + dien mixture (0.10 + 0.15 mol dm^{-3}), (*ii*) additional ^{13}C n.m.r. points in the presence of acetate, and (*iii*) potentiometric titrations.

(*i*) Above about pD 10, the effect of changing the zinc + dien concentrations from 0.20 + 0.44 (where the values of p_i are as shown in Figure 4) to 0.10 + 0.15 mol dm^{-3} is to reduce the proportion of bis complex by *ca.* 0.25, remove uncomplexed dien, and increase the proportion of the mono complex to *ca.* 0.35. This is reflected particularly in δ(C_b) since a low-chemical shift species [ML] (δ 46.82) is formed at the expense of two high-shift species, [ML_2] (δ 48.10) and L (δ 51.78), and there is an overall reduction in chemical shift for the upper plateau region from about 48.5 to 47.6 p.p.m. (squares and dot-dashed line in Figure 1). {If the high pD plateau were associated with the formation of [ML(OH)] it would follow that the only other form present was unprotonated dien (L), since otherwise the chemical shift would change as the pD increased. To give an overall δ(C_b) value for the 0.10 + 0.15 mol dm^{-3} solution of 47.6, the chemical shifts for [ML(OH)] would have to be 45.5

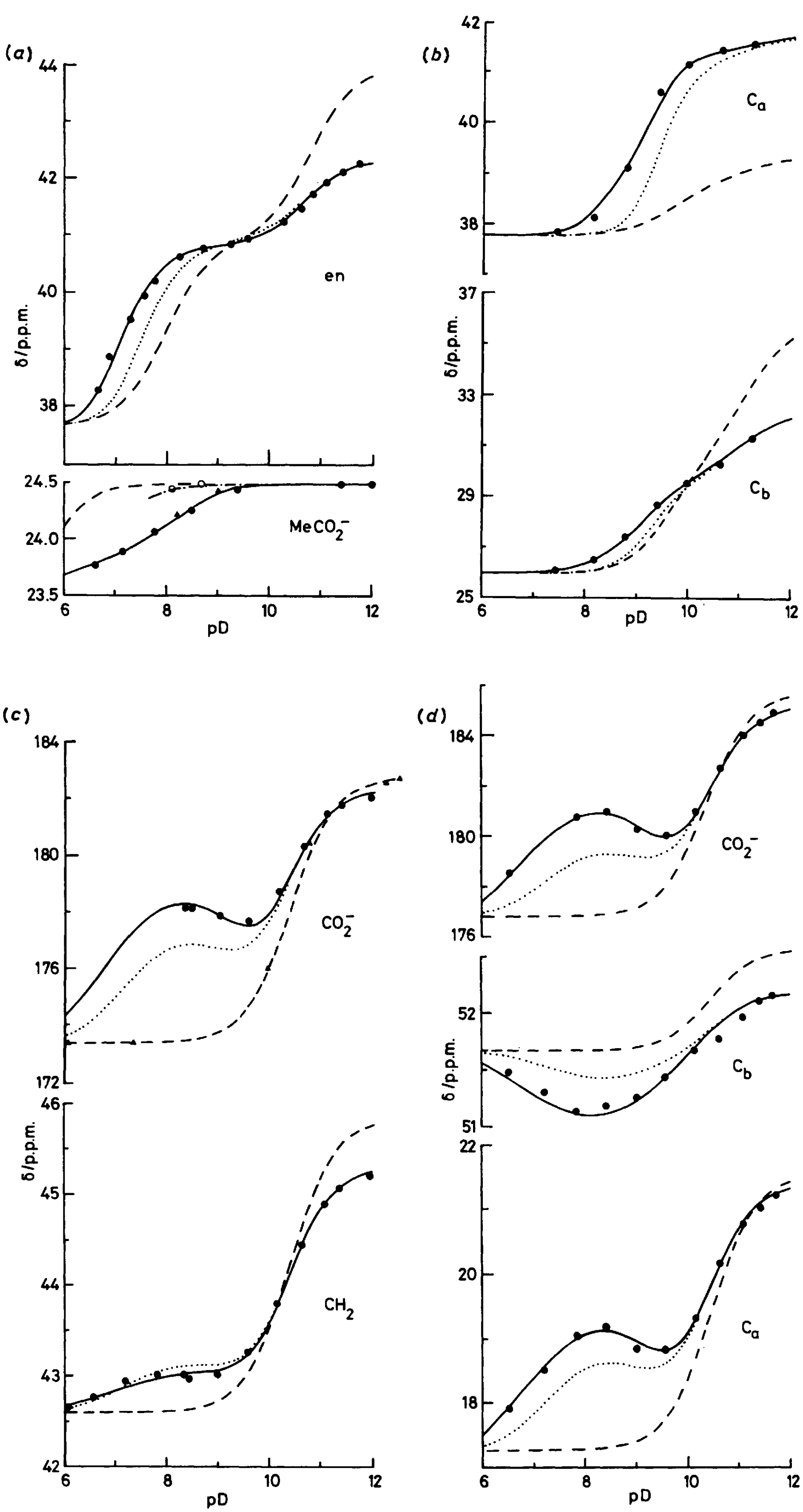

Figure 3. ^{13}C N.m.r. chemical shifts as a function of pD for gly [▲ in (*c*)] and for X in $Zn(NO_3)_2$ + dien + X (●): X = (*a*) en and acetate; (*b*) pn; (*c*) gly; (*d*) ala. Concentrations were 0.20 + 0.44 + 0.20 mol dm^{-3}, respectively, except for pn (when they were 0.10 + 0.15 + 0.10 mol dm^{-3}), and in some cases for acetate [○ and ▲ in (*a*)]

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

		δ(dien)		δ(X)				
Complex		C_a	C_b		In complex	In A	In HA	log K^{ML}_{MLX}
$[Zn(dien)]^{2+}$	[ML]	39.40	46.82			—		9.00[d]
$[Zn(dien)(Hdien)]^{3+}$	[ML(HL)]	39.25	46.70			—		2.70
$[Zn(dien)_2]^{2+}$	$[ML_2]$	39.56	48.10			—		4.30
$[Zn(dien)(en)]^{2+}$	[MLA]	39.30	46.50		40.95	43.98[e]	40.86[e]	4.60
$[Zn(dien)(pn)]^{2+}$	[MLA]	39.50	47.00	C_a	43.80	39.38[f]	38.82[f]	3.30
				C_b	29.30	36.00[f]	30.80[f]	
$[Zn(dien)(MeCO_2)]^+$	[MLA]	38.90	46.10		22.84	24.49[e]	21.50[e]	0.80
$[Zn(dien)(glyO)]^+$	[MLA]	39.35	46.60	CH_2	43.85	45.85[e]	42.60[e]	3.65
				CO_2^-	181.40	182.70	173.40	
$[Zn(dien)(alaO)]^+$	[MLA]	39.20	46.00	C_a	21.00	21.54[e]	17.27[e]	3.60
				C_b	51.00	52.57[e]	51.66[e]	
				CO_2^-	183.70	185.72[g]	176.80[g]	
$[Zn(Hdien)_2(en)]^{4+}$	$[M(HL)_2A]$	39.40	46.50		40.85	43.98[e]	40.86[e]	2.23[h]
$[Zn(Hdien)_2(pn)]^{4+}$	$[M(HL)_2A]$	39.30	46.70	C_a	45.00	39.38[f]	38.82[f]	2.00[h]
				C_b	31.25	36.00[f]	30.80[f]	
$[Zn(Hdien)_2(glyO)]^{3+}$	$[M(HL)_2A]$	39.30	46.45	CH_2	42.95	45.85[e]	42.60[e]	1.30[h]
				CO_2^-	181.40	182.70	173.40	
$[Zn(Hdien)_2(alaO)]^{3+}$	$[M(HL)_2A]$	39.10	46.75	C_a	20.35	21.54[e]	17.27[e]	1.15[h]
				C_b	50.40	52.57[e]	51.66[e]	
				CO_2^-	184.70	185.72[g]	176.80[g]	

[a] The 'best' values for the binary system were determined from 21 data points (Zn + dien, 0.20 + 0.44 mol dm^{-3}), with standard deviations of the experimental chemical shifts from the values calculated on the basis of the parameters listed of 0.052 (C_a) and 0.066 (C_b) p.p.m. For the ternary systems, the numbers of data points (in parentheses) and standard deviations for the ligand X were, respectively: en (15), 0.058; pn (C_a) (7), 0.11; pn (C_b) (7), 0.09; $MeCO_2^-$ (7), 0.02; gly (CH_2) (13), 0.041; gly (CO_2^-) (9), 0.18; ala (C_a) (11), 0.059; ala (C_b) (11), 0.075; and ala (CO_2^-) (10), 0.10. [b] The estimated errors are ±0.1 p.p.m. generally but ±0.2 p.p.m. for MLA (A = $MeCO_2^-$, glyO, or alaO). [c] At 21 ± 1 °C; I various. K^{ML}_{MLX} = [Zn(dien)X]/[Zn(dien)][X] with X = $Hdien^+$, dien, en, pn, $MeCO_2^-$, glyO, or alaO. The estimated errors in log K^{ML}_{MLX} are ±0.1. [d] Value for stability constant of $[Zn(dien)]^{2+}$ (*cf.* refs. 4—7). [e] Data from ref. 10. [f] Data from ref. 2. [g] Data from ref. 3. [h] Formation constant is defined as in footnote *c* (with X = Hen^+, Hpn^+, gly, or ala) although the complex is believed to be the tautomeric form (column 1; see text).

p.p.m. which would require the plateau value for the 0.20 + 0.44 mol dm^{-3} solution to be 49.0 p.p.m. rather than the observed 48.2 p.p.m.}

(*ii*) The solid line in the lower part of Figure 3(*a*) provides an indication of the proportion of acetate which is bound to $[Zn(dien)]^{2+}$ in a solution containing zinc + dien + acetate (0.20 + 0.44 + 0.20 mol dm^{-3}). Comparison of this figure with Figure 4 suggests that, as the pD is raised above 6, the bound $MeCO_2^-$ is gradually replaced by $Hdien^+$, as the solid line approaches the broken one. The effect of increasing the concentration of dien in the mixture to 0.80 mol dm^{-3} would be to lower the pD by which this replacement is complete, since it would increase the competitiveness of $Hdien^+$ over $MeCO_2^-$. The dot-dashed line in Figure 3(*a*) reflects this; it has been computed assuming the parameters listed in Tables 1 and 2 and matches the experimental points (open circles) well. [So as to rule out the possibility that the observed difference in chemical shift might be associated with the rather large ionic strength increase, two spectra were taken of the 0.20 + 0.44 + 0.20 mol dm^{-3} solution to which 1.2 mol dm^{-3} KNO_3 had been added. These are represented by the triangles in Figure 3(*a*) and demonstrate that this effect is minimal.]

(*iii*) The data obtained in the potentiometric titration of a 0.21 mol dm^{-3} solution of dien containing 0.10 mol dm^{-3} zinc are given by the solid circles in Figure 2, and our 'best-fit' computed curve by the solid line. Although the fit (±0.03 cm^3 standard deviation in terms of volume added) is not as good as that for the free ligand (± <0.01 cm^3), the main features of the titration are reproduced well; in particular, the need to incorporate [ML(HL)] in the program is established through a comparison with the curve generated without its inclusion (dotted line) and there is no evidence for the formation of $[Zn(dien)(OH)]^+$. (Note that the titration was taken to a considerably higher pH

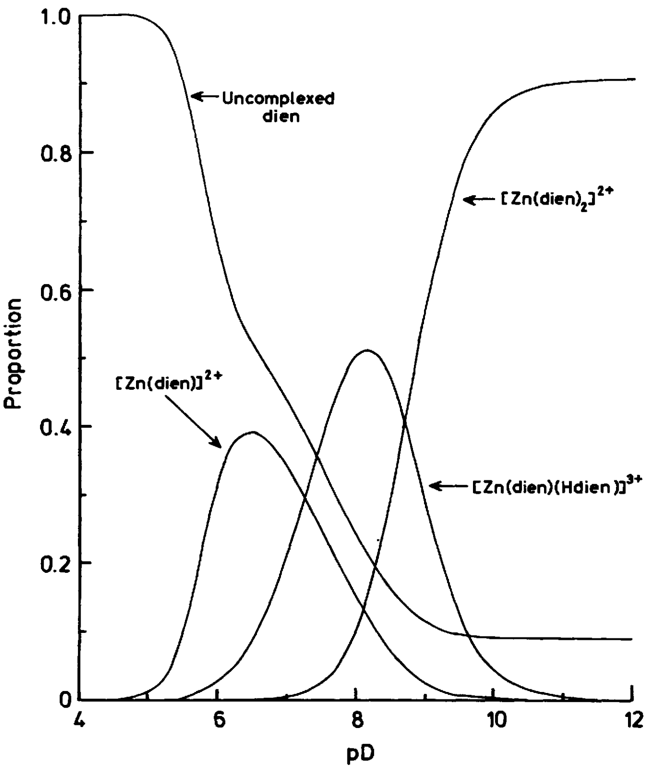

Figure 4. Distribution diagram for the various complexes and uncomplexed dien in Zn (0.20 mol dm^{-3}) + dien (0.44 mol dm^{-3}) solutions

than is usual for potentiometric titrations involving zinc complexes.) The quality of fit is comparable to those obtained [10] for concentrated solutions of other zinc polyamines and is not affected significantly by whether or not the protonated mono complex $[Zn(Hdien)]^{3+}$ is included. {Unfortunately, there is a similar ambiguity with regard to $[Zn(Hdien)]^{3+}$ in the ^{13}C chemical shift profiles and the derived chemical shifts for $[Zn(Hdien)]^{3+}$, 39.20 and 46.70 p.p.m., are very close to those of the other species present, [ML], [ML(HL)], and H_2L (as expected, see below).} The standard deviation is markedly increased by introducing the species $[M(HL)_2]$ (see below).

3. *The* Zn^{2+} + dien + X *Ternary Systems.*—The measured chemical shifts of the carbon atoms of X in mixtures of $Zn(NO_3)_2$ (0.20 mol dm^{-3}), dien (0.44 mol dm^{-3}), and X (0.20 mol dm^{-3}) at different pD are represented by the solid circles in Figure 3 (0.10, 0.15, and 0.10 mol dm^{-3}, respectively, in the case of pn). The solid lines were computed using the formation constants K^{ML}_{MLX} and chemical shifts δ(X) listed in Table 2, and assuming the computed pD profile of the free ligand (broken lines in Figure 3). In the case of bidentate X it is necessary to incorporate parameters for a protonated ternary complex in addition to the expected complexes [Zn(dien)(glyO)]$^+$, *etc.*, [MLA]. This is illustrated in Figure 3, where the dotted lines have been constructed assuming that only [MLA] is formed. In the zinc–tren [3] and –trien [2] ternary systems (tren = 2,2′,2″-triaminotriethylamine, trien = triethylenetetramine) where similar evidence was found for the involvement of protonated forms, the latter were formulated as [ML(HA)], with HA acting as a monodentate ligand. The possibility that the protonated species here is also [ML(HA)] was considered but whereas the points could be fitted for the en system on this basis, those for pn, gly, and ala could not. Comparison with the zinc–dien distribution diagram (Figure 4) shows that the pD range in which the disagreement between observed and calculated chemical shifts is greatest (6—10) is that over which [ML(HL)] is formed. A reasonable possibility for this protonated ternary complex would therefore be [ML(HL)(HA)], formed by addition of HA to [ML(HL)].

The solid lines in Figure 3 agree well with the experimental data but two observations suggest that the additional species is actually the tautomeric form $[M(HL)_2A]$, which is analytically equivalent. In the first place, the formation of gly and ala [ML(HL)(HA)] complexes with log K^{ML}_{MLX} values of 1.30 and 1.15, respectively, would suggest that the carboxylate group had no difficulty entering the inner co-ordination sphere of the metal and therefore that $MeCO_2^-$ should be able to do so too. (Corresponding values for zinc–trien are 0.7, 0.6, and 0.8, respectively.[2]) However, Figure 3(*a*) and the dien profiles (not shown) indicate that no such complex is formed between zinc–dien and $MeCO_2^-$. The other reason concerns the chemical shift of C_a in the pn complex. We have found that the chemical shifts of the α carbon atoms in linear aliphatic polyamines complexed to zinc are considerably larger than those for the unprotonated form of the ligand when these atoms are part of a six-membered ring but not otherwise.[2,8] Signals for C_a in both the unprotonated and protonated ternary complexes of pn with zinc–dien resonate well downfield of pn (δ 43.80, 45.00, and 39.38, respectively), indicating that in both cases the diamine is acting as a bidentate ligand.

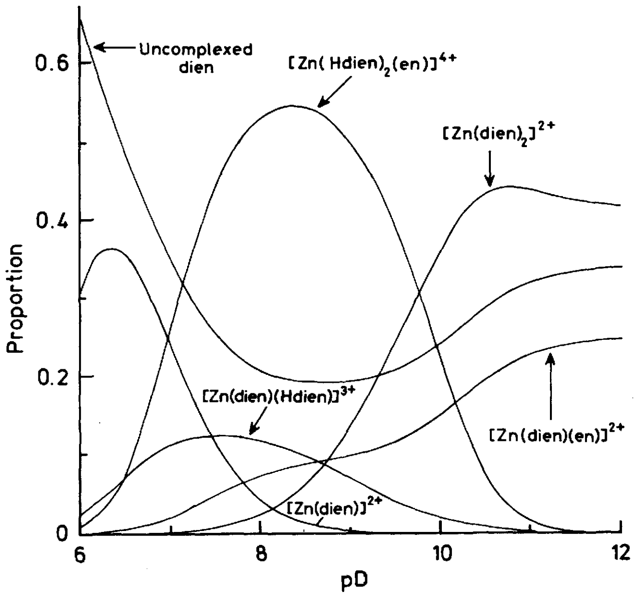

Figure 5. Distribution diagram for the various complexes and uncomplexed dien in $Zn(NO_3)_2$ (0.20 mol dm^{-3}) + dien (0.44 mol dm^{-3}) + en (0.20 mol dm^{-3})

The chemical shift profiles for the C atoms of dien in the Zn + dien + X systems are not shown as they are very similar to those for Zn + dien (Figure 1). A representative distribution diagram, for Zn + dien + en (0.20 + 0.44 + 0.20 mol dm^{-3}), is given in Figure 5.

Discussion

The results reported here provide evidence that the major complexes formed in decimolar solutions containing zinc and an excess of dien (Figure 4) are $[Zn(dien)]^{2+}$, $[Zn(dien)(Hdien)]^{3+}$, and $[Zn(dien)_2]^{2+}$ but not $[Zn(dien)(OH)]^+$. With a comparable concentration of a bidentate ligand X the simple ternary complex $[Zn(dien)A]^{m+}$ is formed, but so also is a doubly protonated species containing two dien and one A molecules per zinc (*cf.* Figure 5) in which the protons are localised on the dien moieties. Neither [ML(HL)] nor the $[M(HL)_2A]$ complexes have been reported previously. Although the mechanism for the formation of $[M(HL)_2A]$ must be conjectural at this stage, the lack of evidence for a significant presence of $[Zn(Hdien)_2]^{4+}$ in the X-free solution and the low concentration of free A at the relevant pH (around 8) suggest that it does not involve the simple addition of A to $[M(HL)_2]$. On the other hand, [ML(HL)] and HA are both major forms near pH 8 and the high lability of the former could easily result in the formation of a precursor complex [ML(HL)(HA)] in which A is bound to the metal by its unprotonated end. An internal proton transfer from HA to one of the primary amino groups of L would be followed (or accompanied) by ring closure of A. Such an intramolecular proton transfer is reasonable on energetic grounds as the microscopic pK_a values of the terminal amino group in dien [19] and HA [20] are all *ca.* 10 and the effect of the bound zinc, while uncertain, is unlikely to be very different for dien and HA. Presumably the main driving force is the relative stability of the octahedrally co-ordinated product in which the Zn^{2+} ion is a member of three separate five-membered rings (two five- and one six-membered when A = pn) and, in particular, the release of the strain which is apparently present [21] in $[Zn(dien)_2]^{2+}$ (see below).

In general, the chemical shifts of the dien carbon atoms in the 12 complexes listed in Table 2 show remarkably little variation, thereby strengthening our previous conclusion [1–3] that there is little, if any, transmission of inductive effects from one part of the co-ordination sphere to another through the zinc atom. If, for the reason discussed below, the single case of C_b in $[ML_2]$ is excepted, the average chemical shifts for C_a and C_b in all the complexes are 39.30 and 46.56 p.p.m., respectively (with standard deviations of 0.17 and 0.28 p.p.m.). These values are close to the averages for the mono- and di-protonated forms of the free ligand (39.9 and 46.7 p.p.m.) and suggest that, to a first approximation, the effect on the ^{13}C n.m.r. chemical shifts in dien of forming a zinc complex is equivalent to half protonating it, as was found with trien[2] and is reported[8] for two of the C atoms in dadn. It also explains why the δ values for [ML(HL)] and $[M(HL)_2A]$ are so close to the others (except C_b in $[ML_2]$) and why it was impossible to obtain evidence from the chemical shifts about the existence of [MHL]. The chemical shifts for X in the ternary complexes are all broadly consistent with those in the zinc–trien[2] and/or –tren[3] complexes.

Four single-crystal *X*-ray structure determinations have been published[21–24] on zinc–dien complexes, of which three relate to the bis complex $[ML_2]$. These involved, respectively, bromide,[21] nitrate,[22] and chloride + perchlorate[23] as the anions, and in each case the $[Zn(dien)_2]^{2+}$ ion was found to contain octahedrally co-ordinated zinc with the ligands arranged meridionally. The dimensions in the cation are very similar and an interesting feature is that the four metal–primary N bonds are significantly longer than the two metal–secondary N bonds, as in the corresponding copper(II) complexes.[23,25] The close similarity between the structures of the bis(dien) complexes of these two metals (and in particular the angular distortions from a regular octahedral geometry) has been ascribed[21] to the constraining influence of the dien ligands, and the existence of so many 'long' zinc–ligand bonds in $[ML_2]$ appears to be indicative of the inter-ring strain mentioned above {and with which the enthalpy of formation of $[Zn(dien)_2]^{2+}$ is consistent[26]}. Moreover, its retention in solution would explain the abnormally high chemical shift found for C_b in $[ML_2]$.

The only other zinc–dien structure to have been reported appears to be that of $[Zn(dien)(bipyam)]^{2+}$ (bipyam = di-2-pyridylamine) in which Ray and Hathaway[24] found that the N atoms are arranged trigonal bipyramidally around the zinc, with the dien secondary nitrogen in one of the axial positions. In this case, the zinc–primary N bond lengths are normal while the zinc–secondary N and the other axial Zn–N bonds are somewhat elongated. Many five-co-ordinate zinc complexes based on the trigonal bipyramid are now known, and the fact that the bond lengths and angles in $[Zn(dien)(bipyam)]^{2+}$ are almost identical to the analogous ones in $[Zn(tren)Y]^+$ (with Y = SCN[27] or Cl,[28] and where Y and the tertiary N are in the axial positions) suggests that this is a stable structure with dien. Certainly, the lack of ternary complex formation between $[Zn(dien)(Hdien)]^{3+}$ and $MeCO_2^-$ (in spite of the favourable charges) is consistent with such a view, and we propose that this configuration is adopted in zinc–dien complexes (with the other equatorial and axial positions occupied by either one bidentate or two monodentate ligands) unless there is a suitably placed chelating group which can impose six-co-ordination on the metal. Such an expansion of the co-ordination sphere would occur quite easily in $[ML_2]$ as only a small movement of the first dien would be needed to incorporate the free end of the second one, to give the *mer* octahedral arrangement. {The alternative trigonal-bipyramidal formulation of $[ML_2]$ with one of the primary amino groups unbound cannot be ruled out, however, since the observed $\delta(C_b)$ value of 48.1 would imply a chemical shift for C_b in the 'open' fragment of *ca.* 52 p.p.m., which is close to the value in free L.} Expansion of the co-ordination sphere would clearly also occur on formation of the diprotonated ternary complex $[M(HL)_2A]$ and this comparatively facile interchange between co-ordination geometries proposed here for the dien complexes of zinc is of particular interest in connection with the suggested[29] role for this metal in enzyme chemistry.

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