Carbon-13 Nuclear Magnetic Resonance Study of Complexes involving Zinc(II) and 2,2′,2″-Triaminotriethylamine†

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Carbon-13 n.m.r. spectra are reported as a function of pH for mixtures of 2,2′,2″-triaminotriethylamine (tren) and zinc nitrate and/or chloride, and of zinc and tren with 1,2-diaminoethane (en), 1,3-diaminopropane (pn), glycine (gly), and L-alanine (ala). Carbon-13 chemical shifts are also reported as a function of pH for tren and L-alanine (carboxylate carbon) alone. The pH profiles have been analysed by computer and the chemical shifts of the methyl, methylene, methine and carboxylate (in the L-alanine complexes only) carbon atoms determined for the following species: tren, $Htren^+$, H_2tren^{2+}, H_3tren^{3+}, $[Zn(tren)(OH)]^+$, $[Zn(tren)(OH_2)]^{2+}$, $[Zn(tren)(en)]^{2+}$, $[Zn(tren)(pn)]^{2+}$, $[Zn(tren)(glyO)]^+$, $[Zn(tren)(alaO)]^+$, $[Zn(tren)(Hpn)]^{3+}$, and $[Zn(tren)(ala)]^{2+}$ [glyO = glycinate(1−), alaO = alaninate(1−)]. Stability constants have also been determined for the ternary complexes. The implications of the results as to the co-ordination geometry of zinc in these complexes and the extent of transmission of inductive effects through the metal are discussed.

No simple spectroscopic technique has been developed for determining the co-ordination geometry of zinc complexes in solution, largely because of the d^{10} configuration of Zn^{2+}. We are examining the possible use of ^{13}C n.m.r. spectroscopy for this purpose and have recently shown[1,2] that it is possible to identify and characterize the separate complexes in a mixture of zinc and one or two organic ligands, even if the complexes are labile on the n.m.r. time-scale: through the least-squares comparison of the chemical shifts of the various carbon atoms in the absence and presence of zinc with computer-simulated pH profiles, it is possible to determine the individual chemical shifts of the non-equivalent C atoms in the various uncomplexed and complexed forms of the ligands, and the stability constants of many of the complexes. Carbon-13 chemical shifts are known[3] to be determined partly by steric ('through space') effects and partly by inductive ('through bonds') effects and if they are to be used to obtain structural information about zinc complexes, it is important to establish the extent to which electronic effects are transmitted from one part of the co-ordination sphere to another through the zinc ion. It is with this aspect that the present paper is primarily concerned.

There is evidence, largely of a thermodynamic nature,[4] that variability of co-ordination number occurs among the complexes of zinc with a series of aliphatic polyamines, but there is little direct structural information about specific amine complexes. Two of the few single-crystal *X*-ray diffraction determinations to have been reported involve zinc complexes with 2,2′,2″-triaminotriethylamine (tren), namely $[Zn(tren)Cl][B(C_6H_5)_4]$[5] and [Zn(tren)(NCS)]SCN.[6] In both cases the geometry of the cation is approximately trigonal bipyramidal, with the tertiary nitrogen of the amine and an anion (respectively Cl^- and NCS^-) in the axial positions. We have recently published[7] *X*-ray diffraction evidence that the trigonal-bipyramidal geometry is retained in a concentrated aqueous solution of $ZnCl_2$ + tren (1:1) and this (together with thermodynamic,[4,8] spectrophotometric[9] and proton n.m.r.[10] evidence) suggests that co-ordinational flexibility is lacking in the complexes of zinc with this ligand. We have therefore chosen to investigate the inductive effects of different axially-bound organic ligands X on the chemical shifts of the C atoms in $[Zn(tren)]^{2+}$ in the expectation that no complications would arise from a change in the zinc co-ordination geometry.

The ^{13}C chemical shifts for aqueous solutions containing 0.22 mol dm^{-3} tren and 0.20 mol dm^{-3} zinc are reported as a function of pD. From a computer fit of this pD profile and that for the free ligand (0.20 mol dm^{-3}) we are able to evaluate the chemical shifts of the two non-equivalent carbon atoms in the following species: tren (L), $Htren^+$, H_2tren^{2+}, H_3tren^{3+}, $[Zn(tren)(OH_2)]^{2+}$, and $[Zn(tren)(OH)]^+$. Exchange between free and complexed tren is slow on the n.m.r. time-scale up to *ca.* pD 9.5 and of comparable rate to the chemical shift difference (in frequency units) above pD 9.5.

The pD profiles of the ^{13}C chemical shifts of the methyl, methylene, and methine carbon atoms in solutions of tren (0.22 mol dm^{-3}), zinc (0.20 mol dm^{-3}), and X (0.20 mol dm^{-3}), where X is 1,2-diaminoethane, 1,3-diaminopropane, glycine, or L-alanine, are also reported, together with those of the carboxylate C atom in the L-alanine system and in L-alanine (0.20 mol dm^{-3}) alone. The chemical shifts for the X ligands have been used to compute the stability constants K^{ML}_{MLX} of the ternary complexes and in all cases the chemical shifts of the tren C atoms in the latter have been determined. All four X ligands form complexes [MLA], while evidence for the formation of complexes [ML(HA)] was found only in the cases of 1,3-diaminopropane and L-alanine (overall charges omitted for clarity). Consideration of the stability constants of the [MLA] complexes suggests that en, pn, glyO, and alaO all bind in a unidentate manner, implying that the co-ordination geometry of the zinc remains trigonal bipyramidal. As was found in a parallel study with triethylenetetramine (trien),[2] the chemical shifts of corresponding C atoms in the zinc complexes are very similar.

Experimental

The ligand tren was isolated from technical-grade trien as the hydrochloride,[11] the regenerated amine being distilled under

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† *Supplementary data available* (No. SUP 56505, 6 pp.): observed chemical shifts for solutions containing tren, tren + Zn, tren + Zn + X. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1986, 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, tren = 2,2′,2″-triaminotriethylamine; ligand X = A (glyO, alaO, en, or pn) or HA (gly, ala, Hen^+, or Hpn^+).

Non-S.I. unit employed: Torr = 133 N m^{-2}.

reduced pressure (127—128 °C at 0.15 Torr). The regeneration step was omitted in later experiments, for which the tren was weighed out as its salt; except for the free ligand at very low pD (where data on other polyamines suggest[12] that interaction between polyprotonated ligand and the nitrate ion might be responsible), the chemical shifts were found to be independent, to within experimental error, of the initial state of the amine. The solutions were made up in D_2O as described previously,[13,14] the pD being calculated by the empirical[15] relationship pD = pH meter reading + 0.40. Most of the n.m.r. spectra were recorded, as before,[13,14] on a JEOL FT-100 spectrometer except that 8K data points were generally accumulated for the ala system to accommodate the wider frequency range needed for the CO_2^- resonance. A few spectra were also recorded on a Bruker WM-200/WB instrument[1] but, while the agreement was good for free tren and at low pD for the Zn^{2+}–tren system, the appearance of the Zn^{2+}–tren spectra in the intermediate exchange region (see below) and some of the chemical shifts obtained with the ternary systems were out of line. We attribute these discrepancies to the substantial degree of r.f. heating caused by the Bruker instrument and its effect on the equilibria involved and have not used the data from these spectra in analysis. Chemical shifts were measured relative to internal 1,4-dioxane (δ 67.71) and are quoted on the δ scale; they are generally estimated to be reliable to ±0.04 p.p.m.

Results

1. The Free Ligands.—The C atoms in pn, ala, and tren are identified as shown below. The measured chemical shifts δ for C_a

pn $NH_2C_aH_2C_bH_2CH_2NH_2$
ala $C_aH_3C_bH(NH_2)CO_2H$
tren $(NH_2C_aH_2C_bH_2)_3N$

and C_b in tren at different pD values are represented by the points in Figure 1. The titration curves were computed from these data by the method used previously,[14] which gave the pK_a values (pK_D^c) and chemical shifts listed in Table 1. Also listed are the first three pK_a values for tren in D_2O predicted on the basis of the application of a constant deuterium isotope effect ΔpK of 0.63 (see ref. 14) to the literature values in H_2O (pK_H^c); in all cases the agreement is good. The agreement is also good between our values of δ for H_3tren^{3+} (37.60 and 51.00) and those of Casy[16] (37.75 and 51.08 p.p.m.). If it is assumed that the three protons in H_3L^{3+} are located entirely on the primary amino groups, the δ values predicted on the basis of our π and π^+ parameters[13] are 37.3 and 52.4 p.p.m. The agreement with the observed values is only moderate, indicating the need to allow for one or more cross-terms and/or a contribution from the tautomer with a protonated tertiary N atom (for which the data are not available). The fourth pK_a does not seem to have been reported, presumably because it is very low: we found that the chemical shifts did not deviate significantly from those of H_3L^{3+} until *ca.* pD 1, suggesting that the pK_a is in the region of 0. The spectral lines for free tren were consistently sharp and of approximately the same height, confirming that exchange between the various protonated forms is rapid on the n.m.r. time-scale.

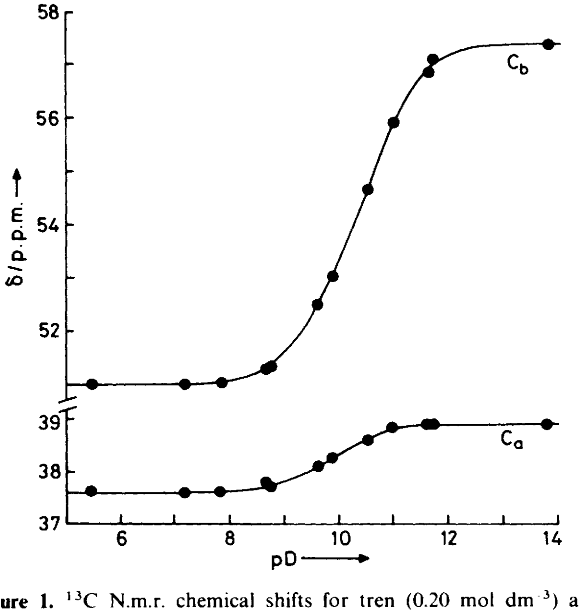

Figure 1. ^{13}C N.m.r. chemical shifts for tren (0.20 mol dm^{-3}) as a function of pD

The triangles in Figure 2(*c*) represent the measured chemical shifts of the carboxylate C atom of free L-alanine, which yielded chemical shifts in alaO and ala of 185.72 and 176.80 p.p.m., respectively. The broken lines in Figure 2 represent the computed pD profiles of the free X ligands (*cf.* refs. 2 and 14).

2. The Zn^{2+} + tren *System.*—The measured chemical shifts for tren + Zn^{2+} (0.22 + 0.20 mol dm^{-3}) at different pD are represented by the points in Figure 3. (The significance of the different symbols is explained below.) The analysis of these data depends on a knowledge of whether exchange between free and complexed tren is rapid on the n.m.r. time-scale and this cannot be determined either from the appearance of the spectra (although, as will be described below, the small variations in relative height of the two peaks do provide useful supporting evidence) or from the chemical shift pD profiles. At first sight the latter suggest slow exchange between free ligand and the aqua and/or hydroxo forms of the 1 : 1 complex (for which we have determined[14] a pK_D of 11.21), but further consideration indicates that this interpretation is unsatisfactory. To help resolve this problem, several additional spectra were recorded with an excess of ligand (> 10%) to provide evidence for the exchange pattern; the results of these are shown in Figure 4. We shall consider in turn (*a*) the exchange pattern below *ca.* pD 9.5, (*b*) the exchange pattern above *ca.* pD 9.5, and (*c*) the possible formation of bis-ligand complexes.

(*a*) At pD values between 7.5 and 9.5 the distribution diagram computed on the basis of published[17,18] pK_a values and stability constants indicates essentially complete conversion of zinc to the 1 : 1 aqua complex as long as tren is in excess; thus, a solution of 0.40 and 0.20 mol dm^{-3} total tren and Zn^{2+}, respectively, should contain *ca.* 0.2 mol dm^{-3} $[Zn(tren)(OH_2)]^{2+}$ and the same amount of free tren. The spectra of these solutions

Table 1. 'Best'[a] ^{13}C chemical shifts[b] (p.p.m.) and pK_a values[c] for tren (L)

	$\delta(L)$	$\delta(HL^+)$	$\delta(H_2L^{2+})$	$\delta(H_3L^{3+})$
C_a	38.90	38.85	38.10	37.60
C_b	57.40	55.15	52.40	51.00
Measured pK_D^c		11.00	10.26	9.17
Calculated[d] pK_D^c		10.87	10.19	9.07

[a] The 'best' values were determined from 12 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 0.035, C_b 0.059. [b] The estimated errors are ±0.1 p.p.m. for L, H_3L^{3+} and ±0.2 p.p.m. for HL^+, H_2L^{2+}. [c] At *ca.* 20 °C; *I* various. The estimated errors are ±0.1. [d] Calculated by adding a deuterium isotope effect ΔpK of 0.63 (ref. 14) to values of pK_H^c from refs. 17 and 18.

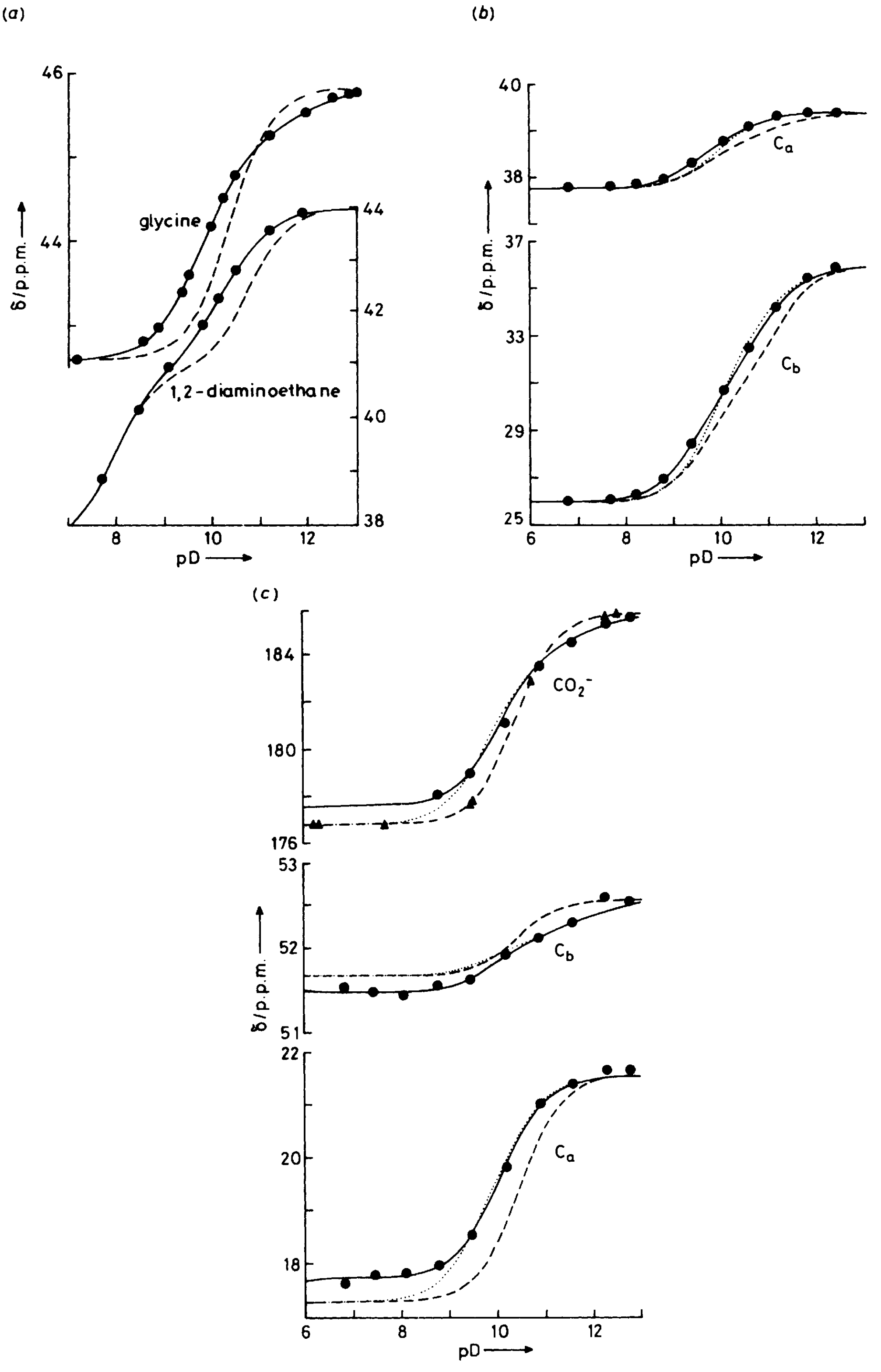

Figure 2. ^{13}C N.m.r. chemical shifts as a function of pD for L-alanine (▲) and for X in Zn(NO$_3$)$_2$ (0.20 mol dm^{-3}) + tren (0.22 mol dm^{-3}) + X (0.20 mol dm^{-3}) (●): X = (*a*) glycine and 1,2-diaminoethane, (*b*) 1,3-diaminopropane, or (*c*) L-alanine

comprised two pairs of sharp peaks with heights similar to that of the internal standard (0.20 mol dm^{-3} 1,4-dioxane). The chemical shift of one member of each pair (attributed to the complex) remained constant while that of the other (the free ligand) moved gradually towards the former as the pD was raised. Coincidence of the two C$_a$ lines occurred at pD $\simeq$ 9.2 and of the two C$_b$ lines at pD $\simeq$ 9.4. There was no sign of line broadening throughout the pD range. Two sharp lines were

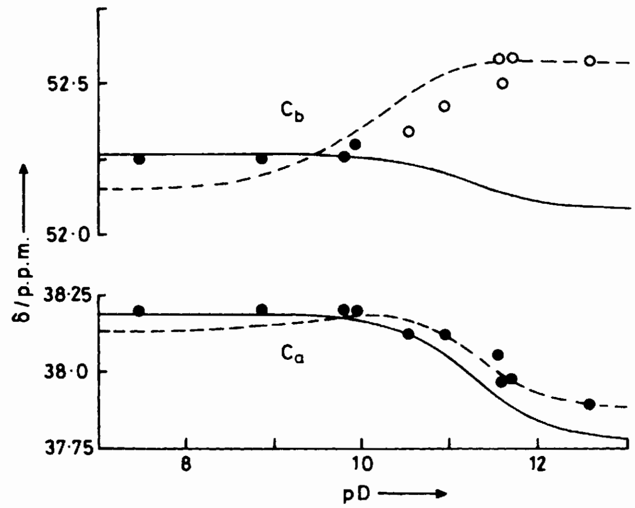

Figure 3. ^{13}C N.m.r. chemical shifts for zinc (0.20 mol dm^{-3}) + tren (0.22 mol dm^{-3}) as a function of pD (see text)

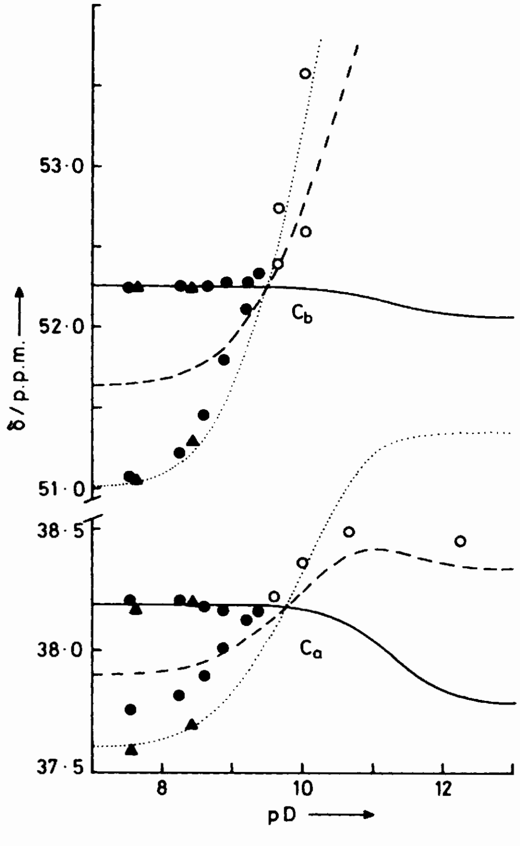

Figure 4. ^{13}C N.m.r. chemical shifts for zinc [0.20 (●, ○) or 0.01 mol dm^{-3} (▲)] + tren [0.40 (●, ○) or 0.02 mol dm^{-3} (▲)] as a function of pD

observed with the 0.22 + 0.20 mol dm^{-3} solutions, with chemical shifts (Figure 3) identical to those of the pD-invariant lines in the 0.40 + 0.20 mol dm^{-3} spectra (Figure 4), while a sharp four-line spectrum was found at pD 5.76 (where the distribution diagram indicates *ca.* 30% dissociation of the complex) with the predicted chemical shifts and relative heights. We therefore conclude that the 0.22 + 0.20 mol dm^{-3} data represent a non-exchanging system below *ca.* pD 9.5.

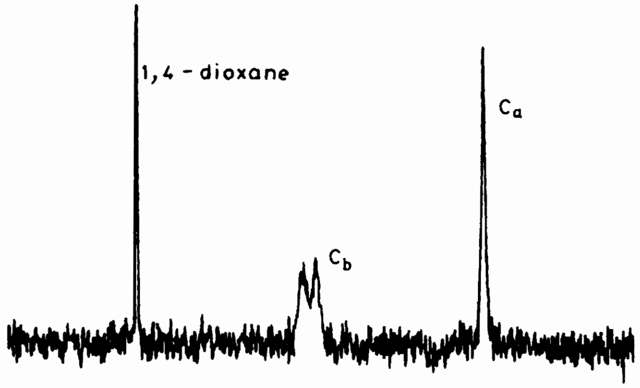

Figure 5. ^{13}C N.m.r. spectrum of a solution containing zinc (0.20 mol dm^{-3}), tren (0.40 mol dm^{-3}), and 1,4-dioxane (0.20 mol dm^{-3}) at pD 10.01

(*b*) Above pD 9.5, exchange broadening occurred to both sets of peaks for the 0.40 mol dm^{-3} tren + 0.20 mol dm^{-3} zinc system and, as with trien,[1] the detailed picture seemed to depend on the difference in δ values for free and complexed forms of the ligand at that pD. For example, at pD 10.01 the values of $|\delta_{free} - \delta_{complexed}|$ are *ca.* 0.2 and 0.9 p.p.m. respectively for C_a and C_b and there is a single C_a signal and two for C_b (Figure 5); all three lines are broadened. The C_b signals coalesce at higher pD but, in contrast to the trien system, the fully-sharpened fast-exchange regime is never attained with either C atom. An attempt to confirm the δ values for $[Zn(tren)(OH)]^+$ by use of a 0.02 + 0.01 mol dm^{-3} tren + zinc solution at pD 11.79 was unsuccessful, but the observation of two major peaks with approximately the chemical shifts predicted for an exchanging system suggests that the exchange rate is not greatly dependent on the concentration of free tren in this pD range. Moreover, the heights of the C_b lines are consistently less than those of the C_a and 1,4-dioxane lines (and therefore indicative of broadening) for the 0.22 + 0.20 mol dm^{-3} tren + Zn^{2+} solutions in the upper pD range (as indicated by the open circles in Figure 3) and we conclude that the data for these concentrations represent an exchanging system above *ca.* pD 9.5.

The dashed lines in Figures 3 and 4 were computed (using the additional data given in Table 2) by the method employed for the ligand, modified to take account of the low- and high-pD forms of the complex {$[Zn(tren)(OH_2)]^{2+}$ and $[Zn(tren)(OH)]^+$; see ref. 14}, and assuming rapid exchange between free and complexed ligand. The solid lines in Figures 3 and 4 assume slow exchange, while the dotted lines in Figure 4 represent the behaviour of the free ligand (*cf.* Figure 1). When allowance is made for the uncertainties accompanying line broadening (open circles), the agreement between the computed and observed chemical shifts is good for both carbon atoms in all cases except the free ligand points in Figure 4 and therefore (with this single possible exception, which is discussed below) provides confirmation of the exchange pattern suggested by the appearance of the spectra.

(*c*) In the trien study,[1] the existence of significant amounts of the bis-ligand complexes $[Zn(trien)(Htrien)]^{3+}$ and $[Zn(trien)_2]^{2+}$ over the pD range 8—12 was demonstrated and their stability constants and chemical shifts determined. From a consideration of the latter, and by comparison [2] with the ternary complexes $[Zn(trien)X]^{n+}$ formed with 1,2-diaminoethane and other small ligands X, it was concluded that these bis complexes contain one ligand moiety bound in quadridentate manner {with essentially the same disposition around the metal as in the aqua, hydroxo, and other $[Zn(trien)]^{2+}$ complexes} and the other bound through only one or two of its N atoms.

Table 2. 'Best'[a] ^{13}C chemical shifts[b] (p.p.m.) and formation constants[c] for $[Zn(tren)]^{2+}$ complexes (see text)

		δ(tren)		δ(X)				log
Complex		C_a	C_b		In complex	In A	In HA	K^{ML}_{MLX}
$[Zn(tren)(OH)]^+$	[ML(OH)]	37.77[d]	52.07[d]			—		—
$[Zn(tren)(ala)]^{2+}$	[ML(HA)]	38.15	52.27	C_a	19.15	21.54[e]	17.27[e]	
				C_b	50.85	52.57[e]	51.66[e]	0.30
				CO_2^-	180.30	185.72	176.80	
$[Zn(tren)(Hpn)]^{3+}$	[ML(HA)]	38.05	52.45	C_a	39.20	39.38[f]	38.82[f]	0.60
				C_b	31.35	36.00[f]	30.80[f]	
$[Zn(tren)(OH_2)]^{2+}$	$[ML(OH_2)]$	38.19[d]	52.26[d]			—		—
$[Zn(tren)(glyO)]^+$	[MLA]	38.18	52.60		45.20	45.85[e]	42.60[e]	1.34
$[Zn(tren)(alaO)]^+$	[MLA]	38.15	52.12	C_a	21.63	21.54[e]	17.27[e]	
				C_b	51.95	52.57[e]	51.66[e]	1.30
				CO_2^-	184.10	185.72	176.80	
$[Zn(tren)(en)]^{2+}$	[MLA]	38.15	52.32		44.10	43.98[e]	40.86[e]	1.26
$[Zn(tren)(pn)]^{2+}$	[MLA]	38.12	52.00	C_a	39.70	39.38[f]	38.82[f]	1.30
				C_b	36.20	36.00[f]	30.80[f]	

[a] The 'best' values for the ternary systems were determined from the following numbers of data points (in parentheses), and the standard deviations of the experimental chemical shifts from the values calculated on the basis of the parameters listed for the small ligand were, respectively: gly (14), 0.030; ala (C_a) (10), 0.093; ala (C_b) (10), 0.063; ala (CO_2^-) (7), 0.21; en (8), 0.029; pn (C_a) (10), 0.033; and pn (C_b) (10), 0.062. [b] The estimated errors are ±0.1 p.p.m. for $[ML(OH_2)]$ and [MLA], and ±0.2 p.p.m. for [ML(OH)] and [ML(HA)]. [c] At *ca.* 20 °C; I various. $K^{ML}_{MLX} = [Zn(tren)X^{n+}]/[Zn(tren)^{2+}][X]$ with X = glyO, alaO, en, pn (K^{ML}_{MLA}) and X = ala, Hpn^+ [$K^{ML}_{ML(HA)}$]. The estimated errors in log K^{ML}_{MLA} are ±0.1 and in log $K^{ML}_{ML(HA)}$ ±0.2. [d] Values for log K_f and pK_a of 14.65 (ref. 17) and 11.21 (ref. 14), respectively, were assumed for $[Zn(tren)(OH_2)]^{2+}$. [e] Data from ref. 14. [f] Data from ref. 2.

Such behaviour is possible also for tren; indeed, on the strength of the reactivity of $[Zn(tren)]^{2+}$ towards en and other small ligands[10] it is to be expected. From (*a*) above, the 'first' (quadridentate bound) tren would be non-exchanging while the 'second' (uni- or bi-dentate bound) tren would behave like en in the $[Zn(tren)(en)]^{2+}$ ternary complex and exchange rapidly, in reflection of the respective stability constants (log K_1 = 14.65, ref. 17, and log K^{ML}_{MLA} = 1.26 for A = en, Table 2). One feature of the ^{13}C n.m.r. behaviour of zinc–trien complexes,[1,2] which seems to apply also to the tren complexes (see below) is that the chemical shifts vary remarkably little in $[Zn(trien)X]^{n+}$ and $[Zn(tren)X]^{n+}$ when the nature of X is varied. Consequently, the chemical shift of the non-exchanging ligand in a mixture of aqua and bis complexes (Figure 4, solid lines) would be essentially the same as that for the aqua complex alone (Figure 3, solid lines), as is observed. On the other hand, the chemical shift of the 'free-ligand' peak would be modified by the contribution from the exchanging component of the bis complex(es). If this were the correct explanation for the observed discrepancy between the experimental points and the 'free-ligand' lines (Figure 4, dotted lines) it would be predicted, on the basis of the rather low stability constants for Zn–tren ternary complexes (Table 2), that the deviation would be greatly reduced by lowering the total tren and zinc concentrations (while maintaining the 2:1 ratio). In confirmation of this, the 'free-ligand' peaks for two solutions containing 0.02 + 0.01 mol dm^{-3} tren + zinc lie, to within experimental error, precisely on the computed line (triangles in Figure 4). In view of the small chemical shift differences and the indication that several bis complexes (with different degrees of protonation of the 'second' ligand) are involved, we have not attempted a detailed characterization of these 2:1 complexes.

3. The Zn^{2+} + tren + X *Ternary systems.*—The measured chemical shifts of the carbon atoms of the X ligand (methylene C only in the case of glycine) in mixtures of X, $Zn(NO_3)_2$, and tren (or tren·3HCl) at different pD values are represented by the circles in Figure 2. The solid lines were computed by the iterative method described previously,[1,14] on the basis of the formation constants K^{ML}_{MLX} and chemical shifts δ(X) listed in Table 2, and assuming the computed pD profile of free X (refs. 2, 14 and broken lines in Figure 2) and the published[19] equilibrium constants for the Zn–tren system. As in the Zn–trien ternary study,[2] it was found necessary for pn and ala to incorporate the parameters for a ternary complex [ML(HA)], as well as [MLA]; failure to do so [dotted lines in Figure 2(*b*) and (*c*)] led in both cases to a significantly poorer fit to the experimental points. {The possibility that these additional complexes are the tautomeric forms [M(HL)A], produced by the reaction of A with a terdentate monoprotonated tren complex $[Zn(Htren)]^{3+}$, is even less likely than in the trien case[2] in view of the absence of any evidence (see above) for the involvement of a partially protonated complex in the Zn–tren system towards low pH}. It is not necessary to invoke the formation of the forms [ML(HA)] to obtain a satisfactory fit for the 1,2-diaminoethane and glycine data [Figure 2(*a*)], although their formation cannot be ruled out since they would not be detectable if the chemical shifts for $[Zn(tren)(Hen)]^{3+}$ and H_2en^{2+}, and for $[Zn(tren)(gly)]^{2+}$ and gly were very similar. The spectral lines for X were consistently sharp and indicative of rapid exchange between complexed and uncomplexed forms. As in the previous paper,[2] we have listed the standard deviations for the C atoms in X calculated from the differences between the observed δ and those computed on the basis of the parameters listed as a guide to the quality of fit of the pD profiles. A representative distribution diagram (for the Zn–tren–pn system) is given in Figure 6.

The measured chemical shifts of the tren C atoms in the solutions of X, zinc, and tren (0.20, 0.20, and 0.22 mol dm^{-3}, respectively) are represented by the points in Figure 7. In general, the spectra were similar in appearance to those of the zinc–tren (0.20 + 0.22 mol dm^{-3}) system at similar pD (see above) and we have analysed the data on the same basis. Thus, as far as the tren moiety is concerned, exchange between free and complexed ligand is assumed to occur above but not below *ca.* pD 10 (although rapid exchange between the various complexed forms occurs over the whole pD range). This is illustrated in Figure 8, which relates to the pn system: the broken lines were computed from the data in Table 2 on the basis of the free-exchange model while the solid lines assume

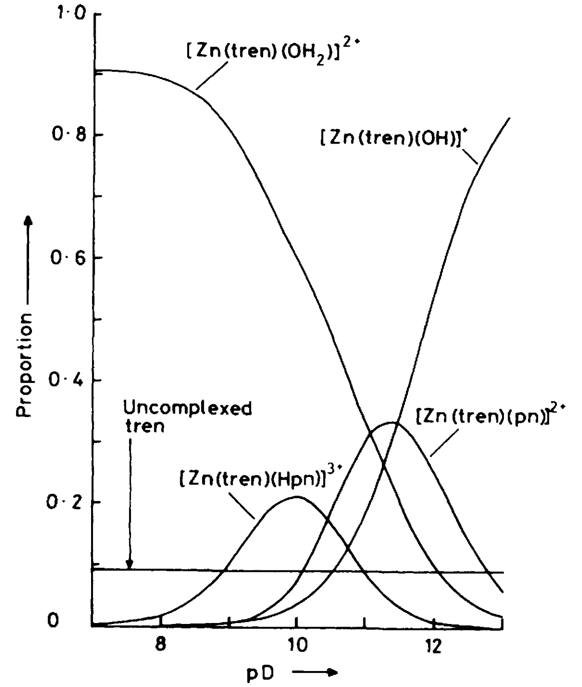

Figure 6. Distribution diagram of the various complexes and uncomplexed tren in $Zn(NO_3)_2$ (0.20 mol dm^{-3}) + tren (0.22 mol dm^{-3}) + pn (0.20 mol dm^{-3})

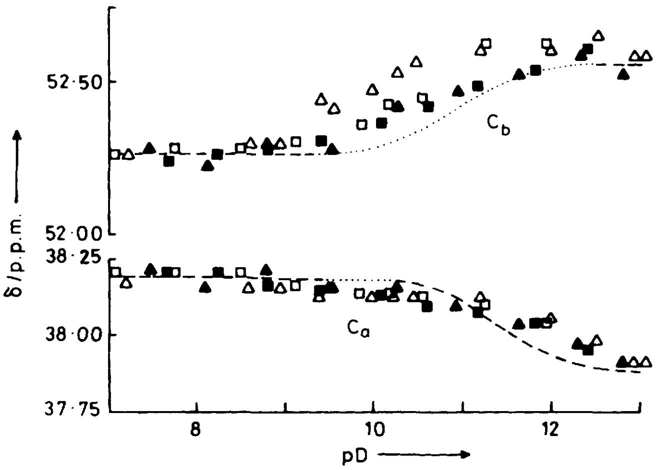

Figure 7. ^{13}C N.m.r. chemical shifts as a function of pD for tren in $Zn(NO_3)_2$ (0.20 mol dm^{-3}) + tren (0.22 mol dm^{-3}) + X (0.20 mol dm^{-3}): X = 1,2-diaminoethane (□), 1,3-diaminopropane (■), glycine (△), or L-alanine (▲)

slow exchange. (The broken lines in Figure 7 are taken from Figure 3 and represent the same extremes for the zinc–tren system, while the dotted portions are empirically-drawn connecting regions.) Although our interpretation is supported by the observation of separate free tren lines in the spectra of solutions containing 0.40 mol dm^{-3} tren + 0.20 mol dm^{-3} zinc and X, we do not regard it as unequivocal since, as with the zinc–tren system, the fully-sharpened fast-exchange regime could not be attained at high pD. Nevertheless, a reinterpretation would have little effect on the δ values quoted for the tren C atoms in Table 2 and none on the values given for the X ligands in the ternary complexes or the stability constants of the latter; it would therefore not affect the conclusion drawn below on the

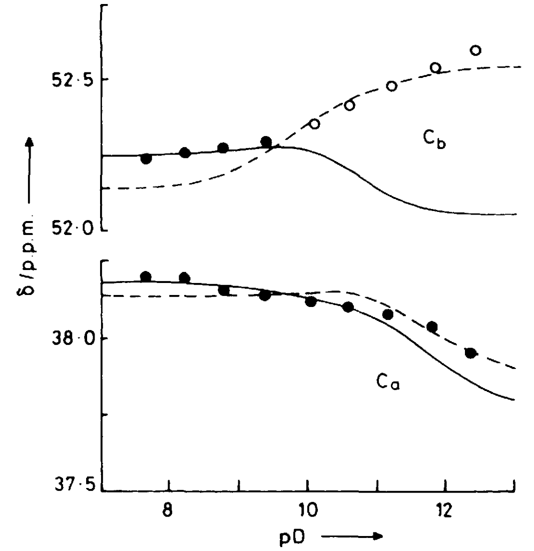

Figure 8. ^{13}C N.m.r. chemical shifts as a function of pD for tren in $Zn(NO_3)_2$ (0.20 mol dm^{-3}) + tren (0.22 mol dm^{-3}) + pn (0.20 mol dm^{-3}). Open circles indicate line broadening (see text)

dependence of chemical shift on inductive effects in these complexes.

Discussion

The most important difference in the ^{13}C n.m.r. behaviour of aqueous solutions of zinc and the isomeric tetramines tren and trien is in their exchange characteristics. The zinc–trien system is rapidly exchanging over the whole pH range in which complexes are formed, with the exception of a narrow band at the low-pH end {corresponding with the formation of significant concentrations of the protonated form $[Zn(Htrien)]^{3+}$} in which serious line-broadening occurs. With zinc–tren, however, exchange is slow at the low-pH end of the stability range for zinc–tren complexes and a changeover to intermediate exchange occurs about halfway through it; rapid exchange is not established, even at the high-pH end, nor is there any exchange broadening at the low-pH end. {Rabenstein and Blakney[10] have also commented on the low exchange rate of $[Zn(tren)]^{2+}$.}The reason for these differences is not obvious and, in particular, it is difficult to see how they can be attributable directly to the variation in stability constant for the 1 : 1 complex since the zinc-3,7-diazanonane-1,9-diamine (dadn)* system is[12] like that of tren in exhibiting slow exchange over a substantial pH range. (Log K_f for Zn^{2+}–trien, –dadn, and –tren = 12.1,[20] 12.8,[21] and 14.7[17] respectively.) Few multidentate ligand-exchange reactions of zinc have been studied,[22] and apparently none involving the replacement of one polyamine with another. However, it has been established[22] with other labile metal ions that the rate-determining step can change with pH and differ between two apparently similar reactions involving the same metal, so perhaps the apparent complexity of the zinc–tetramine exchange behaviour is not surprising. In any event, it would appear to be unwise to make any assumptions about the exchange pattern for other zinc–polyamine complexes solely on the basis of analogy. As with several other polyamines,[12,23] the carbon resonances in tren move progressively upfield with the addition of each proton (Table 1). Both chemical shifts for $[Zn(tren)(OH_2)]^{2+}$ are close to the values for H_2tren^{2+} and

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* The abbreviation 2,3,2-tet was used for this ligand in refs. 13, 14, and 23.

therefore presumably reflect the behaviour of the $[Zn(trien)]^{2+}$ C atoms in being in the middle of the range determined by the unprotonated and fully protonated forms of the free ligand. (As explained above, we have not determined the shifts for H_4-tren^{4+}.)

The values of log K^{ML}_{MLA} for A = en and glyO found here (1.26 and 1.34) are in reasonable agreement with those of Rabenstein and Blakney[10] (1.15 and 1.00). Both these and the values for A = pn and alaO are substantially lower than the 4—6 typically found[2,19] for complexes of these ligands with zinc; in fact, they are similar to (or less than) the incremental stability constants[19] for the zinc complexes of NH_3 and aliphatic monoamines and suggest[2] that all the A ligands are binding in a unidentate fashion. The lower ternary stability constants for the HA forms Hpn^+ and ala [log $K^{ML}_{ML(HA)}$ = 0.60 and 0.30, respectively] than the A forms pn and alO (log K^{ML}_{MLA} = 1.30 in both cases) probably reflect the presence of a protonated N atom at the non-binding end of the ligand in HA which is absent in A. It is premature to discuss in detail the chemical shifts of the X ligands in the ternary complexes since so few zinc shifts have been reported, but it is noticeable that in all cases except one (Table 2) the value of δ(A) in [MLA] is much closer to that of the A form than the HA form of the free ligand. (The exception is C_b in alaO, where it is half-way between the two.) In any event, the present data confirm the previous spectrophotometric[9] and proton n.m.r.[10] evidence that an incoming bidentate ligand is unable to impose on a tren-bound Zn^{2+} ion the octahedral geometry found[24] in complexes of this ligand with Ni^{2+} (an ion of similar radius but different co-ordinational preference). The observation of single C_a and C_b resonances for the non-exchanging tren moiety in the $[Zn(tren)]^{2+}$ complexes supports five-co-ordination, since it suggests that all three chelate rings are equivalent, which they are in the trigonal-bipyramidal arrangement, but not in the octahedral. When it is also considered that (*i*) potentiometric titration of the Zn–tren aqua complex indicates[14] the existence of a single pK_a, (*ii*) ^1H n.m.r. results show[10] that the hydroxo complex contains a single OH^- ion, (*iii*) the molar conductances of dilute solutions of $Zn(tren)(SCN)_2$ and $Zn(tren)Br_2$ are consistent[25] with the presence of 1:1 electrolytes in methanol but 2:1 electrolytes in water (a much better solvent and ligand), and (*iv*) thermochemical measurements suggest[4,8] that the co-ordination number of zinc in its tren complex is five, it is difficult to avoid the conclusion that the trigonal-bipyramidal geometry found in the only crystal structure determinations to have been done[5,6] on Zn–tren complexes is a stable one and that the Zn(tren)X unit (with unidentate X) is retained in solution.

The chemical shifts of the tren carbon atoms in the eight complexes listed in Table 2 show remarkably little variation: treating the data as a single sample yields chemical shifts for C_a and C_b of 38.10 and 52.26 p.p.m., respectively, with standard deviations of 0.13 and 0.19 p.p.m. A similar result was obtained[2] for the three non-equivalent C atoms in 11 zinc complexes of trien, where it was also argued that the geometry adopted by the tetramine in the complexes does not change (in this case it is based on the square pyramid, with the four N atoms of trien coplanar and occupying the basal positions). We concluded[2] that in $[Zn(trien)X]^{n+}$ there is little, if any, transmission of inductive effects from one part of the co-ordination sphere to another through the zinc atom, but this conclusion rested on the assumption that (as indicated by molecular models) the trien C atoms are all remote from X and would therefore not experience significant 'through-space' interaction with it. However, the possibility that 'through-space' and 'through-bonds' effects might be cancelling could not be excluded. The finding of a similar invariance for the chemical shifts of tren in $[Zn(tren)X]^{n+}$ (for which molecular models also indicate that the tren C atoms are remote from X) effectively rules out this possibility and suggests that any large changes in ^{13}C chemical shift which might be found[12] for other closely-related zinc complexes are likely to be steric rather than inductive in origin. In this respect the behaviour of zinc(II) seems to differ from that of diamagnetic transition metals such as cobalt(III) (see, for example, refs. 26 and 27).

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