Carbon-13 Nuclear Magnetic Resonance Study of the Complexes formed between Zinc(II) and Triethylenetetramine

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The ^{13}C n.m.r. spectra are reported as a function of pH for triethylenetetramine (trien) and mixtures of trien and zinc nitrate. At decimolar concentrations the complexes formed are all substitution labile on the n.m.r. time-scale, but separate signals from free and complexed ligand were obtained at millimolar concentrations and low pH. The pH profiles for the exchanging systems have been analysed by computer and the chemical shifts of the three non-equivalent carbon atoms determined for the following species: trien, $Htrien^+$, H_2trien^{2+}, H_3trien^{3+}, H_4trien^{4+}, $[Zn(trien)(OH_2)]^{2+}$, $[Zn(Htrien)]^{3+}$, $[Zn(trien)_2]^{2+}$, $[Zn(trien)(Htrien)]^{3+}$, and $[Zn(trien)(OH)]^+$. The stability constants of $[Zn(Htrien)]^{3+}$, $[Zn(trien)_2]^{2+}$, and $[Zn(trien)(Htrien)]^{3+}$ have also been determined.

There is general agreement that the important role played by zinc in enzyme chemistry is associated with its ability to adopt a co-ordination number of four, five, or six and to change its co-ordination geometry comparatively easily. However, its d^{10} configuration has severely limited the range of techniques available for determining the co-ordination number and this has precluded a systematic investigation of the factors affecting the geometry of its complexes in solution. In view of the widespread use of ^{13}C n.m.r. spectroscopy to provide structural information about various types of organic molecule (*e.g.* the steroids [1]), we have become interested in the possibility of using it to determine the geometry of zinc complexes with organic ligands. A feature which makes it a potentially attractive technique is that, although the chemical shifts are determined partly by inductive effects, they are also affected by steric interactions involving atoms or groups which are geometrically close to the carbon atom in question while being remote from it topologically.[2]

The fact that far fewer ^{13}C n.m.r. spectra have been published for complexes of Zn^{II} (*e.g.* refs. 3—7) than for those of some other diamagnetic metal ions, for example Co^{III} (*e.g.* refs. 8—11), can be largely attributed to two aspects of zinc solution chemistry. In the first place, the complexes are nearly always substitution labile on the n.m.r. time-scale. This reduces the information to be obtained from the spectra by removing structural non-equivalences of chemically equivalent substituents (thereby simplifying the appearance of the spectra) and effectively ruling out spin–spin coupling measurements and selective proton-decoupling experiments. In the second place, solutions made by dissolving the solid complex can usually be studied over only a limited pH range, particularly with the approximately decimolar concentrations needed for routine ^{13}C n.m.r. spectroscopy. This is because zinc forms a very insoluble hydroxide [$pK_{so} \approx 16$ (ref. 12)] which makes it difficult to work in alkaline or even neutral solutions {except at very high pH, where the formation of soluble anionic forms such as $[Zn(OH)_4]^{2-}$ leads to the breakdown of the complex}, while the protonation of the ligand frequently brings about dissociation at low pH. The case of the 3,6-diazaoctane-1,8-diamine (triethylenetetramine, trien) complex illustrates this point well. Although the stability constant of $[Zn(trien)]^{2+}$ is comparatively high [$\lg K_f = 12.1$ (ref. 12)], the computed distribution diagram for a 0.2 mol dm^{-3} solution of the complex indicates that it would be *ca.* 15% dissociated at pH 6.5 and *ca.* 80% dissociated at pH 5.5, while $Zn(OH)_2$ would precipitate out at pH $\gtrsim$ 8.5. A way of extending the available pH range is to use an excess of the ligand but the analysis must then reflect the fact that the measured chemical shifts are the weighted averages of contributions from all the species present, namely, one or more complexes and the uncomplexed form(s) of the ligand. The published results suggest that zinc-complexation shifts are comparable in size (a few p.p.m.) to those observed when the free ligands are protonated and this encouraged us to pursue the technique in spite of the experimental obstacles.

There was another reason for doing so. For some time, we have been using fast reaction techniques to measure the kinetics of ternary complex formation at substitution-labile metal ions with the aim of quantifying the effects of charge, nature of ligating groups, co-ordination number, *etc.* (*cf.* ref. 13), but in several cases with zinc complexes we found it difficult to reconcile our results with the distribution diagrams constructed on the basis of published [12] stability constants. Because of the lack of spectroscopic possibilities with Zn^{II}, these stability constants have nearly all been determined by potentiometric titration, but the non-specific nature of this technique means that there must sometimes be ambiguity over the interpretation of the data and the presence of important species can be overlooked. With ^{13}C n.m.r. spectroscopy, on the other hand, it should be possible to identify the separate complexes, even in rapidly exchanging systems, since the chemical shifts of the various carbon atoms reflect their different environments in the individual species present. The aim of the present paper is to demonstrate, with the Zn^{2+}–trien system, that this is indeed the case and, by a detailed consideration of the variation of chemical shift with pH to determine the chemical shifts for the five complexes involved and the stability constants of three of them. Two of these complexes, $[Zn(trien)_2]^{2+}$ and $[Zn(trien)(Htrien)]^{3+}$, are rather unstable and could only have been detected with difficulty at the comparatively low concentrations generally used in potentiometry, while there is disagreement in the literature over the possible existence of the third, $[Zn(Htrien)]^{3+}$.

We report the ^{13}C chemical shifts for aqueous solutions containing 0.3 mol dm^{-3} trien and 0.2 mol dm^{-3} zinc as a function of pD. From a computer fit of this pD profile and that for the free ligand (0.3 mol dm^{-3}) we are able to evaluate the chemical shifts of the three non-equivalent carbon atoms in the following species: trien, $Htrien^+$, H_2trien^{2+}, H_3trien^{3+}, H_4trien^{4+}, $[Zn(trien)(OH_2)]^{2+}$, $[Zn(Htrien)]^{3+}$, $[Zn(trien)_2]^{2+}$, $[Zn(trien)(Htrien)]^{3+}$, and $[Zn(trien)(OH)]^+$. {The use of the molecular formulae $[Zn(trien)(OH_2)]^{2+}$ and $[Zn(trien)(OH)]^+$ for the low- and high-pH forms of the principal mono complex

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Supplementary data available (No. SUP 56417, 3 pp.): observed chemical shifts for solutions containing trien. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1985, Issue 1, pp. xvii—xix.

will be justified in future papers.[14]} Confirmation of the chemical shifts for the complexes was obtained by using higher and lower trien:zinc ratios at selected pD values; in addition, it was possible to find conditions at low concentration where the exchange process is slow enough to permit the observation of separate signals from free (partially protonated) ligand and $[Zn(trien)(OH_2)]^{2+}$.

Experimental

The solutions were made up in D_2O as described previously;[15,16] the pD was calculated using the empirical[17] relationship pD = (meter reading) + 0.40. Most of the n.m.r. spectra were recorded at *ca.* 20 °C with a JEOL FT100 spectrometer[15,16] but some were recorded on a Bruker WM-200/WB spectrometer, when typically 16K data points were accumulated over a frequency range of 3.5 kHz with 250 scans. Significantly radio frequency (r.f.) heating occurred with the Bruker as a result of the proton decoupling but, when allowance was made for the effect of this on the relevant chemical equilibria, the agreement between the spectra obtained on the two machines was excellent. In some cases (notably with solutions containing Zn and trien at low pH) samples run on the Bruker developed a red, green, or yellow colouration. The origin of this was not established but it appeared to have no effect on the ^{13}C n.m.r. spectra; we attribute it to the presence of a slight impurity in the trien which is converted at higher temperatures into a highly coloured form. Chemical shifts are estimated to be reliable to ±0.04 p.p.m.; they were measured relative to 1,4-dioxane (δ 67.71) but are quoted on the δ scale.

Analysis

The non-equivalent C atoms in trien are identified as follows: $NH_2C_aH_2C_bH_2NHC_cH_2CH_2NHCH_2CH_2NH_2$. The measured chemical shifts δ of the C atoms in trien at different pD values are represented by the points in Figure 1. The titration curves were computed from these data by the method described for the ligand *N*-(2-aminoethyl)propane-1,3-diamine in ref. 16, which yielded the pK_a values (pK_{D^c}) and chemical shifts listed in Table 1. Also quoted are the pK_a values for trien in D_2O predicted on the basis of the literature values for trien in water (pK_{H^c}) and application of a uniform deuterium-isotope effect, $\Delta pK = 0.63$ (see ref. 16); in all cases the agreement is good. The agreement between our values of δ for H_4trien^{4+} (36.50, 44.45, and 45.80) and those of Casy[18] (36.51, 44.47, and 45.82) is also good.

The measured chemical shifts for trien + zinc (0.3 and 0.2 mol dm^{-3}, respectively) at different pD values are represented by the points in Figure 2. The solid lines were computed by the method used for the ligand, modified to take account of the various complexes (see ref. 16 and Discussion section), and assuming the computed pH profile of the free ligand (Figure 1 and dashed lines in Figure 2). Additional spectra were obtained with trien + zinc at concentrations of 0.2 + 0.2 and 0.4 + 0.2 mol dm^{-3} in the pD ranges 5—7 and 8—11, respectively, giving the points shown in Figure 3. Given the assignments[15] of the unprotonated (L) and fully protonated (H_4L^{4+}) forms of trien,

Table 1. 'Best' ^{13}C chemical shift[a] (in p.p.m.) and pK_a values[b] for trien (L) (see text)

(*a*) Chemical shifts

	δ(L)	$\delta(HL^+)$	$\delta(H_2L^{2+})$	$\delta(H_3L^{3+})$	$\delta(H_4L^{4+})$
C_a	40.95	40.30	39.40	38.30	36.50
C_b	51.80	49.60	47.20	45.80	45.80
C_c	48.77	48.00	47.80	46.90	44.45

(*b*) pK_a

Measured	pK_{D^c}	10.65	9.96	7.50	4.30
Calculated[c]	pK_{D^c}	10.55	9.88	7.63	4.48

[a] The estimated errors are ±0.1 p.p.m. The 'best' values were determined from 23 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 0.064, C_b 0.089, and C_c 0.055 p.p.m. [b] At *ca.* 20 °C; various *I*. The estimated errors (see also footnote *a*) are ±0.1. [c] Based on the average values of pK_{H^c} from refs. 19 and 24, and H. B. Jonassen, R. B. LeBlanc, A. W. Meibohm, and R. M. Rogan, *J. Am. Chem. Soc.*, 1950, **72**, 2430; R. L. Pecsok, R. A. Garber, and L. D. Shields, *Inorg. Chem.*, 1965, **4**, 447; D. C. Weatherburn, E. J. Billo, J. P. Jones, and D. W. Margerum, *Inorg. Chem.*, 1970, **9**, 1557.

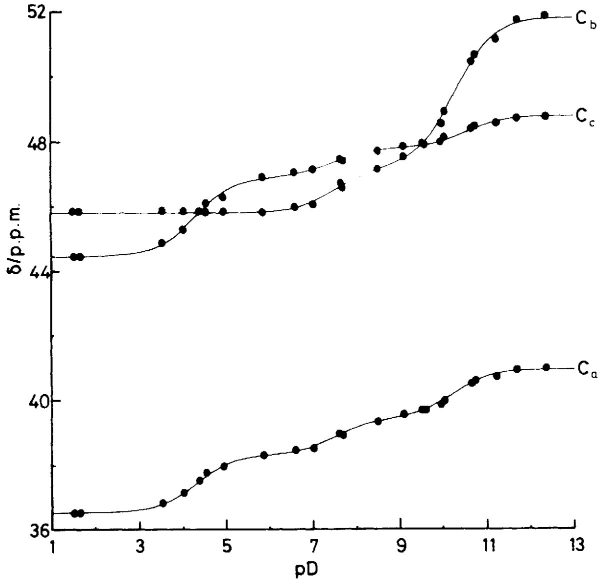

Figure 1. ^{13}C N.m.r. chemical shifts for trien as a function of pD

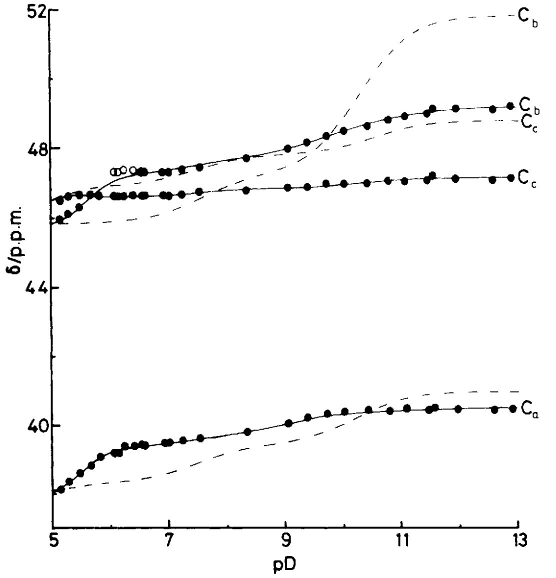

Figure 2. ^{13}C N.m.r. chemical shifts for $Zn(NO_3)_2$ (0.2 mol dm^{-3}) + trien (0.3 mol dm^{-3}) as a function of pD (see text). Values represented by open circles have been omitted from the standard deviation calculation (Table 2)

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

	$[ZnL(OH_2)]^{2+}$	$[ZnL(OH)]^+$	$[Zn(HL)]^{3+}$	$[ZnL_2]^{2+}$	$[ZnL(HL)]^{3+}$
$\delta(C_a)$	39.90	40.25	38.85	40.45	41.00
$\delta(C_b)$	48.00	47.85	46.10	49.40	48.50
$\delta(C_c)$	46.40	46.32	46.50	47.50	46.90
lg K_f					
measured	12.10[c]	9.74[c,d]	6.70[e]	2.18[f]	1.33[f]
literature	12.10[g]	9.74[d,h]	7.2[e,i]		

[a] The estimated errors are ±0.1 p.p.m. {0.2 p.p.m. for $[Zn(HL)]^{3+}$}. The 'best' values were determined from 28 (C_a, C_c) or 24 (C_b) 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 0.051, C_b 0.065, and C_c 0.042 p.p.m. [b] At *ca.* 20 °C; various *I*. The estimated errors (see also footnote *a*) in lg K_f are ±0.2. [c] Assumed value. [d] pK_a value for $[ZnL(OH_2)]^{2+}$. [e] $K_f = [Zn(HL)]/[Zn][HL]$. [f] $K_f = [ZnLX]/[ZnL][X]$ with X = L or HL^+. [g] Refs. 19—22. [h] Ref. 16. [i] Refs. 19 and 22.

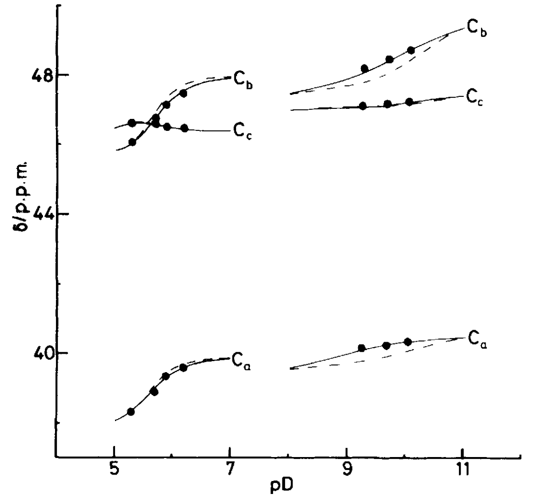

Figure 3. ^{13}C N.m.r. chemical shifts for $Zn(NO_3)_2$ (0.2 mol dm^{-3}) + trien (0.2 mol dm^{-3} at $5 < pD < 7$; 0.4 mol dm^{-3} at $8 < pD < 11$) as a function of pD (see text)

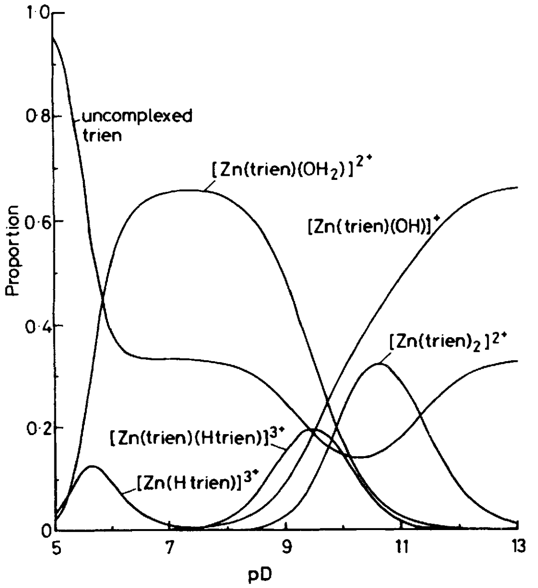

Figure 4. Distribution diagram for the various complexes and uncomplexed trien in Zn (0.2 mol dm^{-3}) + trien (0.3 mol dm^{-3}) solution

it is possible to assign the lines in the rapidly exchanging ligand + complex system unequivocally. In the first place, those of the latter system approach the free-ligand lines as the pD is reduced below 6 (Figure 2) and the complex $[Zn(trien)(OH_2)]^{2+}$ dissociates (Figure 4). (An analogous trend at high pD was also demonstrated but the points have not been included in Figure 2 as the dissociation occurs outside the range of reliable pD measurements, *i.e.* at pD $\gtrsim$ 13.) Secondly, the 'cross-over' at around pD 6 could be demonstrated experimentally (see below). Thirdly, it would not be possible to obtain the level of agreement between calculated and observed shifts seen in Figures 2 and 3 if the assignments were incorrect, given the large chemical shift changes with pD and the large and varying concentrations of free ligand.

The three spectral lines for free trien 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. For the zinc-containing solutions, above about pD 7 the resonances were also uniformly sharp and indicative of rapid exchange between the complex(es) and free ligand. Exchange broadening occurred in the pD range 5—7, but it interfered with the measurements only in the case of the C_b resonance just above the 'cross-over' point (where the C_b signal appears as a shoulder on the much more intense C_c line). The varying heights of the C_a, C_b, and C_c lines at $5 < pD < 7$ could be rationalised simply in terms of the relative differences in δ value for the free and complexed forms of trien at the given pD value, without the need to assume that different parts of the complex(es) have different labilities. Thus, for example, at pD 6.6 (and concentrations of zinc and trien of 0.2 and 0.3 mol dm^{-3}) the approximate values of $|\delta_{free} - \delta_{complexed}|$ are 1.5, 2.1, and 0.5 p.p.m., respectively, for C_a, C_b, and C_c while the degree of line broadening [Figure 5(*a*)] is $C_b > C_a \gg C_c$. The exchange process is sufficiently slow at low concentrations and pD values to permit the (partial) resolution of the free and complexed peaks [Figure 5(*b*)]; in all cases, the resonances are consistent with the shifts computed from the spectra of decimolar solutions (Tables 1 and 2).

The precision with which the chemical shifts and stability constants for the various complexes can be determined depends on several factors, notably the maximum proportion of the species obtainable and the differences between its chemical shifts and those of the other species present in the appropriate pD range. The limits quoted in Tables 1 and 2 are estimated errors. As a guide to the quality of fit of the pD profiles we have also listed the number of spectra used and the standard deviations for the various C atoms reported (calculated from the differences between the observed δ values and those computed on the basis of the parameters listed).

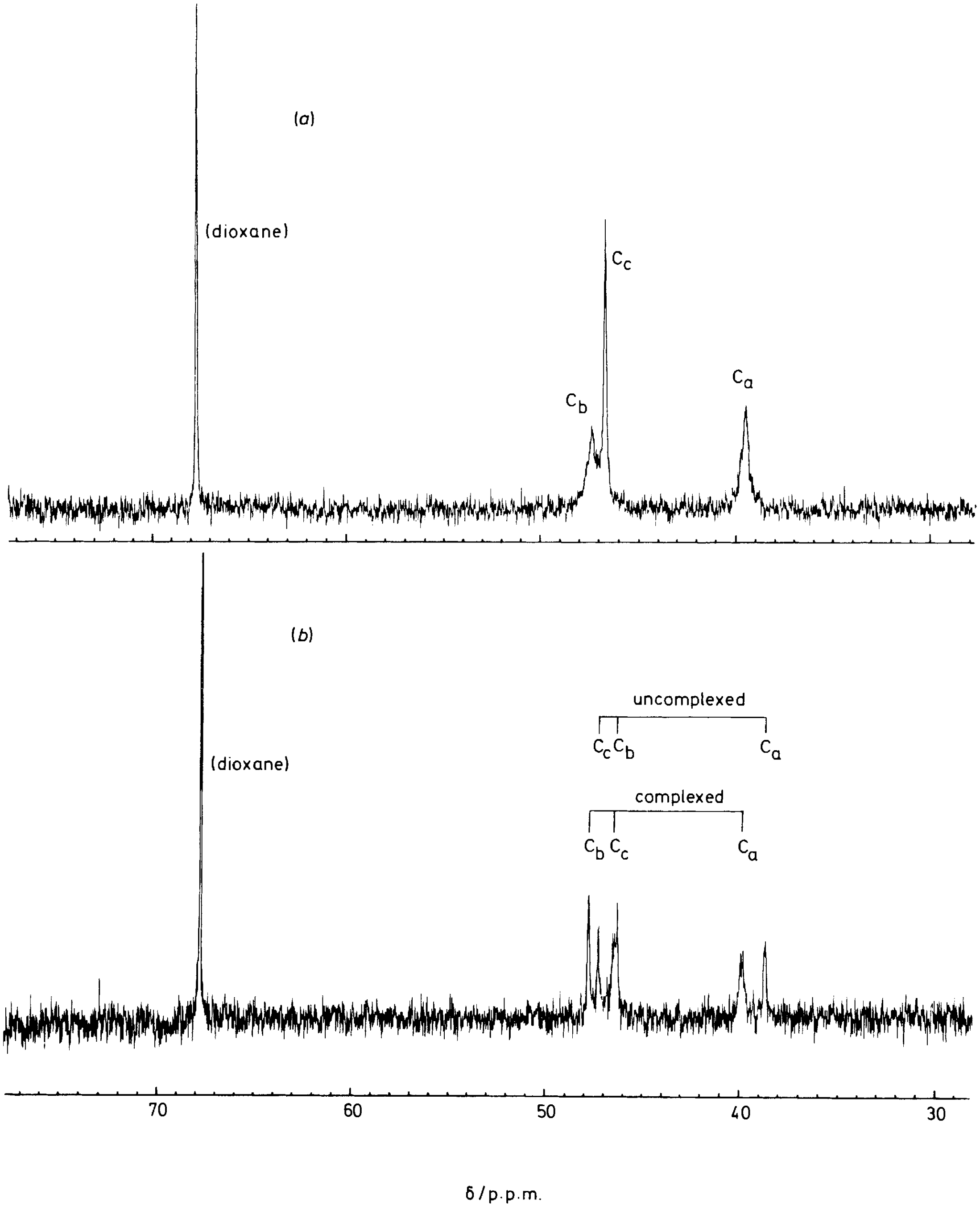

Figure 5. ^{13}C N.m.r. spectra of zinc–trien solutions: (*a*) 0.2 mol dm^{-3} $Zn(NO_3)_2$ and dioxane, 0.3 mol dm^{-3} trien at pD 6.60; (*b*) 2.5 × 10^{-3} mol dm^{-3} $Zn(NO_3)_2$, 5.0 × 10^{-3} mol dm^{-3} trien and dioxane at pD 6.78

Discussion

There have been four determinations of the stability constant(s) of the complex(es) formed between zinc and trien in water[19–22] and, while there is good agreement that the principal 1:1 complex $[Zn(trien)]^{2+}$ has a lg K_f of about 12.1, there is no consensus about even the nature of any other species formed. Schwarzenbach[19,23] attributes a slight deviation from the theoretical titration curve to the formation of a protonated complex $[Zn(Htrien)]^{3+}$, as do Anderegg and Bläuenstein[22] [and also McBryde and Powell,[24] who studied the system in aqueous dioxane (50:50 v/v)]: all three groups report a lg K_f of about 7. On the other hand, Reilley and Schmid[21] make no reference to $[Zn(Htrien)]^{3+}$ while Jonassen *et al.*[20] say they found no evidence for its formation. Evidence for the involvement of a higher complex is provided in only one study[20] but it is not possible to determine the formula(e) or stability constant(s) from the data given. It is noteworthy that none of these papers mentions the acidic dissociation of co-ordinated water in $[Zn(trien)]^{2+}$ which we have recently demonstrated.[16]

The quality of fit between our experimental ^{13}C n.m.r. points and the computed pD profiles is significantly improved if it is assumed that $[Zn(Htrien)]^{3+}$, $[Zn(trien)_2]^{2+}$, and $[Zn(trien)(Htrien)]^{3+}$ are formed in addition to $[Zn(trien)(OH_2)]^{2+}$ and

$[Zn(trien)(OH)]^+$. Preliminary pD profiles for the Zn:trien = 2:3 system, computed on the basis of only the last two complexes (not shown in Figure 2), appeared to deviate from the experimental points in the pD regions 5—6.5 and 8—11, which are where $[Zn(Htrien)]^{3+}$ and the bis complexes, respectively, might be expected to form. To confirm that this deviation was real, we ran spectra in the same pD ranges but at Zn:trien ratios of 1:1 and 1:2, respectively, under which conditions the relative contributions of these additional species would be enhanced. The pD profiles computed on the assumption that the only complexes formed are $[Zn(trien)(OH_2)]^{2+}$ and $[Zn(trien)(OH)]^+$ (Figure 3, dashed lines) reproduce the experimental data for C_a and C_b poorly, while those computed on the basis that all five complexes are involved (solid lines) match the data much better, as do the solid lines in Figure 2 for the 2:3 ratio. We therefore conclude that $[Zn(Htrien)]^{3+}$, $[Zn(trien)_2]^{2+}$, and $[Zn(trien)(Htrien)]^{3+}$ are formed with the stability constants and chemical shifts listed in Table 2. These were evaluated by the iterative procedure outlined above, assuming the literature values of lg K_f and pK_a for $[Zn(trien)(OH_2)]^{2+}$.

The carbon resonances in trien move progressively upfield with the addition of each proton (Table 1) and we have recently used[25] the relative sizes of the steps in the titration curves to determine the order in which the amino-groups are protonated. The chemical shifts for $[Zn(trien)(OH_2)]^{2+}$ all lie towards the middle of the range determined by the unprotonated and fully protonated forms of the free ligand. This is not surprising since the partial positive charge on the amino-groups provided by the zinc cation is likely to be a major factor determining the ^{13}C shifts in the complexed ligand: a charge of +2 is distributed among the four nitrogens and any other co-ordinating atom, giving an effective charge on each N of approximately $+\frac{1}{3}$ to $+\frac{1}{2}$. The low stability constants for $[Zn(trien)_2]^{2+}$ and $[Zn(trien)(Htrien)]^{3+}$ with respect to the mono complex and, in general, the changes in chemical shift on passing from $[Zn(trien)(OH_2)]^{2+}$ to the bis complexes are consistent with the second trien and $Htrien^+$ acting as unidentate ligands (assuming[14] the retention of quadridentate co-ordination by the first trien). In $[Zn(Htrien)]^{3+}$ the difference in behaviour of C_a and C_b {large upfield shifts relative to $[Zn(trien)(OH_2)]^{2+}$} and C_c (little change) presumably reflects the fact that protonation occurs entirely at the primary nitrogens, since it has been established[15] that the chemical shifts of the carbon atoms in aliphatic polyamines are determined primarily by the state of protonation of the two nearest amino-groups. The similarity between the shifts for $[Zn(trien)(OH_2)]^{2+}$ and $[Zn(trien)(OH)]^+$ is noteworthy and argues against the significant transmission of inductive effects through the zinc atom. This contrasts with the position for complexes of cobalt(III) (see, for example, refs. 4, 9, 11, and 26) and suggests that it would be unwise at this stage to try to deduce the geometry of zinc complexes on the basis of results[27] obtained with the complexes of diamagnetic transition-metal ions such as cobalt(III).

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References

1 W. B. Smith, *Annu. Rep. NMR Spectrosc.*, 1978, **8**, 199.
2 J. B. Stothers, 'Carbon-13 NMR Spectroscopy,' Academic Press, New York, 1972; F. W. Wehrli and T. Wirthlin, 'Interpretation of Carbon-13 NMR Spectra,' Heyden, London, 1976; G. C. Levy, R. L. Lichter, and G. L. Nelson, 'Carbon-13 Nuclear Magnetic Resonance Spectroscopy,' 2nd edn., Wiley, New York, 1980.
3 B. J. Fuhr and D. L. Rabenstein, *J. Am. Chem. Soc.*, 1973, **95**, 6944.
4 O. W. Howarth, P. Moore, and N. Winterton, *J. Chem. Soc., Dalton Trans.*, 1974, 2271.
5 M. J. Farmer, O. W. Howarth, and P. Moore, *J. Chem. Soc., Dalton Trans.*, 1976, 1445.
6 N. W. Alcock, N. Herron, and P. Moore, *J. Chem. Soc., Dalton Trans.*, 1978, 1282.
7 H. Lakusta, C. M. Deber, and B. Sarkar, *Can. J. Chem.*, 1980, **58**, 757.
8 K. D. Gailey, K. Igi, and B. E. Douglas, *Inorg. Chem.*, 1975, **14**, 2956.
9 N. Juranić, M. B. Ćelap, D. Vučelić, M. J. Malinar, and P. N. Radivojša, *Inorg. Chem.*, 1980, **19**, 802.
10 C. J. Hawkins, R. H. Holm, J. A. Palmer, and D. L. Traficante, *Aust. J. Chem.*, 1982, **35**, 1815.
11 G. R. Brubaker and D. W. Johnson, *Inorg. Chem.*, 1982, **21**, 2223.
12 L. G. Sillén and A. E. Martell, 'Stability Constants of Metal-Ion Complexes,' The Chemical Society, London, 1964; supplement 1, 1971.
13 D. N. Hague, in 'Chemical Relaxation in Molecular Biology,' eds. I. Pecht and R. Rigler, Springer, Heidelberg, 1977, p. 84.
14 S. P. Dagnall, D. N. Hague, and A. D. Moreton, *J. Chem. Soc., Dalton Trans.*, submitted for publication.
15 S. P. Dagnall, D. N. Hague, and M. E. McAdam, *J. Chem. Soc., Perkin Trans. 2*, 1984, 435.
16 S. P. Dagnall, D. N. Hague, M. E. McAdam, and A. D. Moreton, *J. Chem. Soc., Faraday Trans. 1*, 1985, 1483.
17 R. G. Bates, 'Determination of pH, Theory and Practice,' Wiley, New York, 1964.
18 A. F. Casy, *J. Pharm. Pharmacol.*, 1981, **33**, 333.
19 G. Schwarzenbach, *Helv. Chim. Acta*, 1950, **33**, 974.
20 H. B. Jonassen, G. G. Hurst, R. B. Le Blanc, and A. W. Meibohm, *J. Phys. Chem.*, 1952, **56**, 16.
21 C. N. Reilley and R. W. Schmid, *J. Elisha Mitchell Sci. Soc.*, 1957, **73**, 279.
22 G. Anderegg and P. Bläuenstein, *Helv. Chim. Acta*, 1982, **65**, 913.
23 G. Schwarzenbach, *Helv. Chim. Acta*, 1950, **33**, 947.
24 W. A. E. McBryde and H. K. J. Powell, *Can. J. Chem.*, 1979, **57**, 1785.
25 S. P. Dagnall, D. N. Hague, and M. E. McAdam, *J. Chem. Soc., Perkin Trans. 2*, 1984, 1111.
26 J. Mason, *Adv. Inorg. Chem. Radiochem.*, 1979, **22**, 199.
27 See, for example, G. H. Searle, S. F. Lincoln, S. G. Teague, and D. G. Rowe, *Aust. J. Chem.*, 1979, **32**, 519.

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