Carbon-13 Nuclear Magnetic Resonance Study of Ternary Complexes involving Zinc(II) and Triethylenetetramine†

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The ^{13}C n.m.r. spectra are reported as a function of pH for mixtures of triethylenetetramine (trien) and zinc nitrate with acetic acid, glycine (gly), L-alanine (ala), 1,2-diaminoethane (en), and 1,3-diaminopropane (pn) and for pn alone. The pH profiles for these rapidly-exchanging systems have been analysed by computer, and the chemical shifts of the methyl, methylene, and methine carbon atoms and the stability constants determined for the following species: $[Zn(trien)(MeCO_2)]^+$, $[Zn(trien)(gly)]^{2+}$, $[Zn(trien)(ala)]^{2+}$, $[Zn(trien)(Hen)]^{3+}$, $[Zn(trien)(Hpn)]^{3+}$, $[Zn(trien)(glyO)]^+$, $[Zn(trien)(alaO)]^+$, $[Zn(trien)(en)]^{2+}$, and $[Zn(trien)(pn)]^{2+}$ [glyO = glycinate(1 −), alaO = L-alaninate(1 −)]. 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.

It is generally agreed that a major feature of the solution chemistry of zinc, and one which is largely responsible for its important role in enzyme chemistry, is the ability of this metal to adopt a co-ordination number of four, five, or six and to change its co-ordination geometry comparatively easily. Unfortunately, its d^{10} configuration has precluded the direct determination of co-ordination number in all but a few cases and no generalisations are available about the factors affecting the geometry of these complexes in solution. We have become interested in the possibility of using ^{13}C n.m.r. spectroscopy to provide structural information about zinc complexes with organic ligands since chemical shifts in many classes of compound are known[1] to be subject to steric ('through space') effects associated with atoms or groups which are geometrically close to a particular carbon atom although remote from it topologically. However, ^{13}C shifts are also determined by inductive ('through bonds') effects and it is therefore important to establish at an early stage the extent to which these electronic effects may be transmitted from one part of the co-ordination sphere to another through the zinc ion itself.

There is a body of evidence, much of it thermodynamic,[2] that variability of co-ordination number occurs among the complexes of zinc with a range of aliphatic polyamines, but direct structural information about specific amines is sparse. One of the few single-crystal *X*-ray structure determinations has been[3] on [Zn(trien)I]I (trien = triethylenetetramine) and we have therefore chosen to study complexes of trien (L) first. Under normal conditions zinc complexes of this ligand in water are labile on the n.m.r. time-scale, but we have recently shown[4] that ^{13}C chemical shifts may be analysed by computer to determine the composition of zinc–trien solutions and to provide reliable chemical shifts for the individual complexes present. The purpose of the present paper is to report the extension of this analytical application of ^{13}C n.m.r. spectroscopy to the (labile) ternary complexes of $[Zn(trien)]^{2+}$, [ML], with a number of small organic ligands X and the determination of their stability constants K^{ML}_{MLX}.

The pD profiles of the ^{13}C chemical shifts of the methyl, methylene, and methine carbon atoms in solutions of trien (0.22 mol dm^{-3} with X = 1,3-diaminopropane, otherwise 0.3 mol dm^{-3}), zinc nitrate (0.2 mol dm^{-3}), and X (0.2 mol dm^{-3}), where X is 1,2-diaminoethane, 1,3-diaminopropane, glycine, L-alanine, or acetic acid, are reported, together with that of 1,3-diaminopropane alone (0.2 mol dm^{-3}). The X ligand shifts have been used to compute the stability constants of the ternary complexes and in all cases the chemical shifts of X and trien in the complexes have been determined unequivocally. With $[Zn(trien)]^{2+}$ all the ligands X except acetic acid form complexes [MLA] and [ML(HA)] (overall charges omitted for clarity). Consideration of the stability constants of the [MLA] complexes, together with other evidence, suggests that en, pn, glyO, and alaO all bind in a bidentate manner. The chemical shifts of the corresponding C atoms of trien in most of the complexes studied here and previously[4] are very similar. The implications of these 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.

Experimental

1,3-Diaminopropane (B.D.H.; b.p. 137—139 °C at 760 Torr) was purified by distillation; the other amines and $Zn(NO_3)_2$ were prepared, and the solutions made up in D_2O, as described previously.[5] The pD was calculated using the empirical[6] relationship pD = pH meter reading + 0.40. The n.m.r. spectra were recorded at *ca.* 20 °C with a JEOL FT-100 spectrometer[5] using internal 1,4-dioxane as reference. The chemical shifts are quoted on the δ scale. As before,[5] the collection of data in samples containing gly, ala, and acetic acid was restricted to the CH_n (n = 1—3) carbons.

Results

The C atoms in pn, ala, and trien are identified as shown below.

pn	$NH_2C_aH_2C_bH_2CH_2NH_2$
ala	$C_aH_3C_bH(NH_2)CO_2H$
trien	$NH_2C_aH_2C_bH_2NHC_cH_2CH_2NHCH_2CH_2NH_2$

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† *Supplementary data available* (No. SUP 56504, 5 pp.): observed chemical shifts for solutions containing trien, Zn, and 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, trien = triethylenetetramine (3,6-diazaoctane-1,8-diamine); ligand X = A (glyO, alaO, $MeCO_2^-$, en, or pn) or HA (gly, ala, Hen^+, or Hpn^+).

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

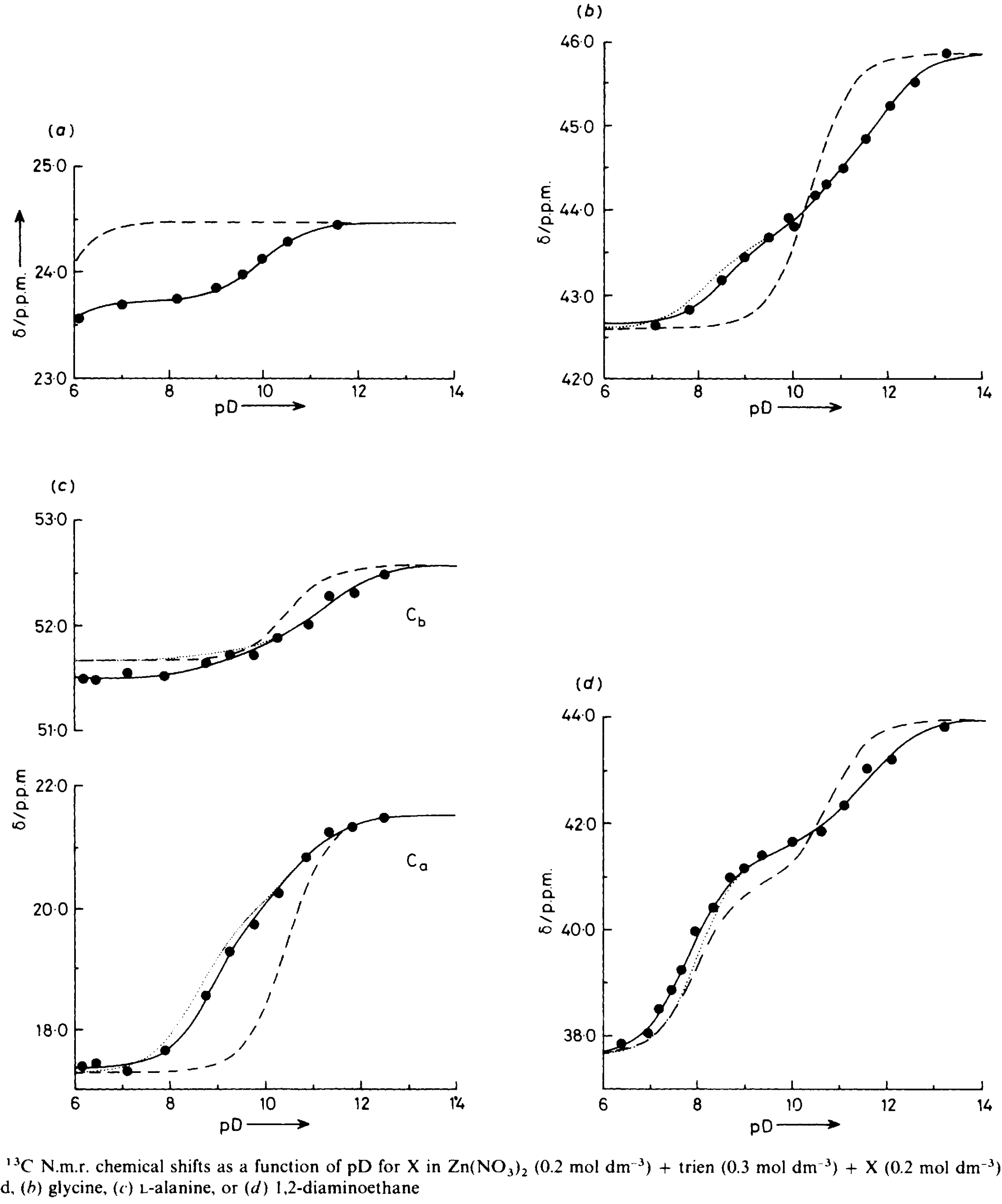

Figure 1. ^{13}C N.m.r. chemical shifts as a function of pD for X in $Zn(NO_3)_2$ (0.2 mol dm^{-3}) + trien (0.3 mol dm^{-3}) + X (0.2 mol dm^{-3}): X = (*a*) acetic acid, (*b*) glycine, (*c*) L-alanine, or (*d*) 1,2-diaminoethane

The measured chemical shifts δ of the methyl, methylene, and methine C atoms of X in mixtures of X, $Zn(NO_3)_2$, and trien at different pD values are represented by the points in Figures 1 and 2. The measured chemical shifts of the C atoms of trien for the Zn–trien–en system are shown in Figure 3; the pD variations for the trien C atoms in the other ternary systems were similar to these and are not shown. The solid lines were computed by the iterative method described previously,[4,5] on the basis of the formation constants K^{ML}_{MLX} and chemical shifts δ(X) listed in the Table, and assuming the computed pD profile of free X (ref. 5 and dashed lines in Figures 1 and 2) and the equilibrium constants for the Zn–trien system used previously.[4] The triangles in Figure 2 represent the measured chemical shifts of the C atoms of free pn, which yielded chemical shifts in pn, Hpn^+, and H_2pn^{2+} of 39.38, 38.82, and 37.76 p.p.m. for C_a and 36.00, 30.80, and 25.97 p.p.m. for C_b, together with pK_a values of 11.15 and 9.65. [The pK_a values compared well with those (11.27 and 9.51) predicted on the basis of the literature values[7] in H_2O and application of a deuterium isotope effect[5] Δp*K* of 0.63.] As in the previous paper,[4] we have listed the standard deviations for the various C atoms calculated from the differences between the observed δ and those computed on the basis of the parameters listed (Table), as a guide to the quality of fit of the pD profiles.

One noteworthy feature of the analysis of all the systems involving a bidentate X ligand (*i.e.*, glycine, L-alanine, 1,2-

diaminoethane, or 1,3-diaminopropane) was the need to incorporate the parameters for a ternary complex formed from the HA form {*i.e.* [ML(HA)]} as well as one formed from the A form (*i.e.* [MLA]). Failure to do so led in all cases to a significantly poorer fit to the experimental points, as shown by the dotted lines in Figures 1 and 2. {Consideration of the magnitudes of the stability constants suggests that these additional complexes are unlikely to be the tautomeric forms [M(HL)A], produced by the reaction of A with the terdentate monoprotonated trien complex $[Zn(Htrien)]^{3+}$. This conclusion is strengthened by the fact that the chemical shifts of C_a and C_b in the trien moiety are much closer to the values for $[Zn(trien)(OH_2)]^{2+}$, $[Zn(trien)(OH)]^{+}$, and $[Zn(trien)A]^{n+}$ (n = 1 or 2) than to those[4] for $[Zn(Htrien)]^{3+}$.} The formation of complexes with the HA forms of the ligands X is, in fact, to be expected since there are several reports in the literature of the involvement of analogous complexes in Zn–X binary systems. For example, Krishnan and Plane[8] reported the formation of such complexes with glycine, Carlson and Brown[9] found evidence that uni-, bi-, and ter-dentate 1:1 complexes are formed with histidine at various pH, while Rabenstein and Libich[10] demonstrated that zinc binding to di-, tri-, and tetraglycine occurs at the C-terminal end at pH 1—4 (in addition to the N-terminal binding occurring at higher pH). A typical distribution diagram (in terms of trien) showing the major complexes and uncomplexed ligand for the Zn–trien–en system is given in Figure 4.

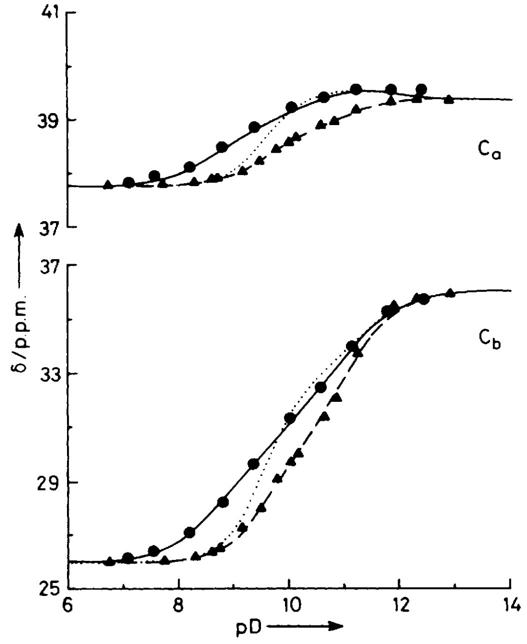

Figure 2. ^{13}C N.m.r. chemical shifts as a function of pD for pn alone (▲) and for pn in $Zn(NO_3)_2$ (0.2 mol dm^{-3}) + trien (0.22 mol dm^{-3}) + pn (0.2 mol dm^{-3}) (●)

The spectral lines for trien and X were (with the exception of

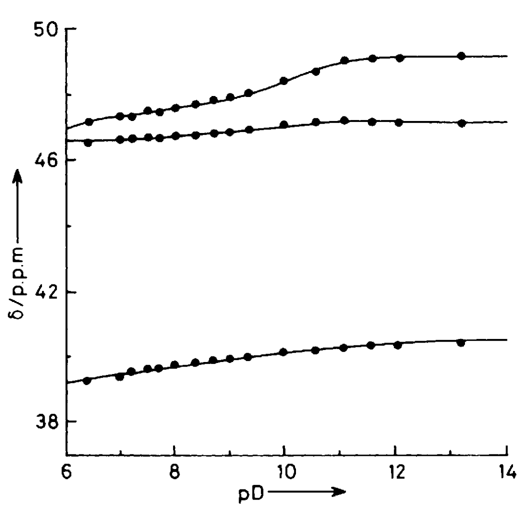

Figure 3. ^{13}C N.m.r. chemical shifts as a function of pD for trien in $Zn(NO_3)_2$ (0.2 mol dm^{-3}) + trien (0.3 mol dm^{-3}) + en (0.2 mol dm^{-3})

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

			δ(trien)			
Complex		C_a	C_b	C_c	δ(X)	log K^{ML}_{MLX}
$[Zn(trien)(OH)]^{+}$	[ML(OH)]	40.25[d]	47.85[d]	46.32[d]	—	—
$[Zn(trien)(MeCO_2)]^{+}$	[MLA]	39.85	47.70	46.50	22.80	0.8
$[Zn(trien)(gly)]^{2+}$	[ML(HA)]	39.85	47.70	46.50	42.75	0.7
$[Zn(trien)(ala)]^{2+}$	[ML(HA)]	39.70	47.40	46.50	17.50(C_a) 51.20(C_b)	0.6
$[Zn(trien)(Hen)]^{3+}$	[ML(HA)]	40.00	47.60	46.10	41.10	0.6
$[Zn(trien)(Hpn)]^{3+}$	[ML(HA)]	40.25	47.65	46.10	39.40(C_a) 31.35(C_b)	1.6
$[Zn(trien)(OH_2)]^{2+}$	$[ML(OH_2)]$	39.90[d]	48.00[d]	46.40[d]	—	—
$[Zn(trien)(glyO)]^{+}$	[MLA]	39.85	48.00	46.65	44.00	2.8
$[Zn(trien)(alaO)]^{+}$	[MLA]	39.95	47.90	46.65	21.40(C_a) 51.80(C_b)	2.5
$[Zn(trien)(en)]^{2+}$	[MLA]	39.85	48.10	46.60	41.90	2.7
$[Zn(trien)(pn)]^{2+}$	[MLA]	39.70	47.75	46.20	40.65(C_a) 36.00(C_b)	2.2

[a] The 'best' values for the ternary systems were determined from the following numbers of sets 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 C_a, C_b, C_c of trien and X were, respectively: acetic acid (8), 0.082, 0.059, 0.040, 0.024; gly (14), 0.029, 0.059, 0.041, 0.050; ala (12), 0.057, 0.076, 0.036, 0.051, 0.039; en (16), 0.045, 0.051, 0.037, 0.074; and pn (10), 0.027, 0.078, 0.033, 0.037, 0.072. [b] The estimated errors are ±0.1 p.p.m. for the complexes [MLA] and ±0.2 p.p.m. for the complexes [ML(HA)]. [c] At *ca.* 20 °C; I various. $K^{ML}_{MLX} = [Zn(trien)X^{n+}]/[Zn(trien)^{2+}][X]$, with X = $MeCO_2^-$, glyO, alaO, en, pn (K^{ML}_{MLA}) and X = gly, ala, Hen^+, 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] Data from ref. 4.

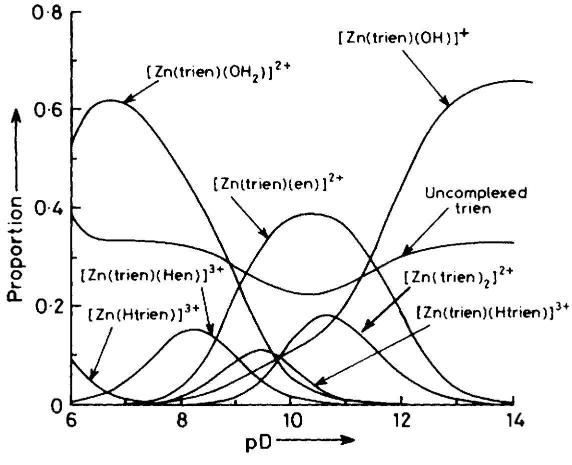

Figure 4. Distribution diagram for the various complexes and uncomplexed trien in $Zn(NO_3)_2$ (0.2 mol dm^{-3}) + trien (0.3 mol dm^{-3}) + en (0.2 mol dm^{-3})

some trien lines below about pD 7) consistently sharp and of approximately the correct relative heights for the respective concentrations, confirming that exchange was rapid on the n.m.r. time-scale.

Discussion

It is well established that the stability constants of complexes formed between a particular metal ion and a series of ligands containing similar binding groups tend to increase steadily with the denticity of the ligand. For 1:1 complexes of Zn^{2+} (aq) in which bonding is through amino or carboxylate groups the value of log K_1 is typically[7] in the range 1.0—2.5 for unidentate ligands and 4.0—6.0 for bidentate ligands, with N-binding ligands forming rather more stable complexes than O-binding ligands. For example, the values of log K_1 for $MeCO_2^-$, NH_3, en, glyO, and alaO are[7] *ca.* 1.3, 2.4, 5.9, 5.4, and 5.2, respectively. The second stability constant K_2 is usually a little lower than the first but the distinction between uni- and bidentate binding is equally clear; log K_2 for the unidentate $MeCO_2^-$ and NH_3 are *ca.* 0.8 and 2.4, and for the bidentate en, glyO, and alaO respectively 5.0, 4.5, and 4.3. Far fewer stability constants have been reported for mixed complexes of zinc than of some other metals (*e.g.* Cu^{2+}, ref. 11) but from those that have there seems to be little to distinguish $K^{\mathrm{ML}}_{\mathrm{MLA}}$ from the K_2 value for A, provided the total denticity of the two ligands L and A does not exceed five. [It may be noted that on statistical grounds the formation of the mixed-ligand species is slightly favoured[12,13] over the higher complex (K_n, $n > 1$)with a single ligand.] Thus, for example, Gergely and Sóvágó[14] and Daniele and Ostacoli[15] have recently provided data from which it is possible to evaluate $K^{\mathrm{ML}}_{\mathrm{MLA}}$ for a bi- or ter-dentate ligand L and A = en, glyO, or alaO. Typical values of log $K^{\mathrm{ML}}_{\mathrm{MLA}}$ are as follows: 5.21 for L = *N,N*-dimethylethylenediamine (dmen), A = en; 4.75 for L = en, A = glyO; 4.87 for L = dmen, A = glyO; 4.58 for L = L-histidine, A = glyO; and 4.27 for L = L-histidine, A = alaO. A similar picture is found for the binding of en and glyO to the dizinc complex of 1,4-bis[bis(2-aminoethyl)aminomethyl]benzene, for which log $K^{\mathrm{ML}}_{\mathrm{MLA}}$ are,[16] respectively, 5.63 and 5.05 for the addition of the first A and 5.31 and 4.65 for the addition of the second. These values are all close to the respective values for log K_2 and it seems safe to conclude that A is acting as a bidentate ligand in every case.

In general, the third stability constants K_3 for zinc show a greater variability than the first or second, although for en, glyO, and alaO K_3 is much less than K_1 or K_2 (log K_3 = 2.0, 2.5, and 2.0, respectively). Low values of log $K^{\mathrm{ML}}_{\mathrm{MLA}}$ have also been reported[17] for the reaction of en and glyO with $[Zn(tren)]^{2+}$ (tren = 2,2′,2″-triaminotriethylamine) (1.15 and 1.00, respectively) and are found here (Table) for the reaction of en, pn, glyO, and alaO with $[Zn(trien)]^{2+}$ (2.7, 2.2, 2.8, and 2.5 respectively). In view of the similarity between these incremental stability constants and the typical values found for unidentate ligands it is tempting to conclude that the additional ligand is binding in a unidentate fashion. However, this is not the only possible reason for a low stability constant. Another explanation is that the co-ordination number of the metal is six and for steric or electronic reasons some or all of the bonds are rather longer and therefore weaker than in the lower complexes. Two pieces of evidence support the latter interpretation in the case of $[Zn(en)_3]^{2+}$ and it is suggested, in view of the similarity of the equilibrium constants, that the same conclusion may be drawn for the other tris complexes mentioned and, with respect to the A ligand, for the ternary complexes of en, pn, glyO, and alaO with $[Zn(trien)]^{2+}$. {We shall argue in the following paper[18] in favour of the alternative explanation for the low values of $K^{\mathrm{ML}}_{\mathrm{MLA}}$ for the $[Zn(tren)]^{2+}$ ternary complexes.} From a study of the Raman spectra of zinc–en solutions, Krishnan and Plane[19] concluded that there are no unco-ordinated N atoms in solutions in which the major complex is $[Zn(en)_3]^{2+}$. Fujita *et al.*[20] came to the same conclusion following an *X*-ray investigation of a concentrated aqueous solution containing Zn^{2+} and en in the molar ratio 1.0:3.2. The latter group were also able to determine the mean Zn–N distance in the tris complex: at 2.28 Å it is significantly longer than the 2.1 Å commonly found[21] in zinc complexes with aliphatic amines. It is interesting to note that a similar explanation can be advanced for the fact that the second stability constant for the zinc complex of the terdentate ligand diethylenetriamine (dien) is markedly lower than the first [log K_1 = 8.9, log K_2 = 5.5 (ref. 22)] since it has been established in three single-crystal structure determinations that the co-ordination number of the metal in $[Zn(dien)_2]^{2+}$ is six, with average Zn–N(primary) distances of, respectively, 2.23, 2.25, and 2.20 Å (refs. 23—25), and we have ^{13}C n.m.r. evidence[26] that the conformation is retained in solution. Such weak bonding has also been invoked[27] in discussions of the possible role of zinc in enzyme reactions.

Lack of suitable data for comparison makes it premature to discuss in detail the chemical shifts of the X ligands in the ternary complexes but the fact that for both en and glyO the values for $[Zn(trien)A]^{n+}$ [n = 2 (en) or 1 (glyO)] (41.9 and 44.0 p.p.m., respectively) are closer to those[26] for $[Zn(dien)A]^{n+}$ (41.0 and 43.7 p.p.m.) and $[Zn(aepn)A]^{n+}$[aepn = *N*-(2-aminoethyl)propane-1,3-diamine;* 40.8 and 43.3 p.p.m.], where the A ligand is almost certainly bidentate, than to those[18] for $[Zn(tren)A]^{n+}$ (44.0 and 45.2 p.p.m.), where the evidence suggests that it is unidentate, supports our interpretation of the low values of $K^{\mathrm{ML}}_{\mathrm{MLA}}$ with L = trien. Further support is provided by two additional features of the results (Table). The chemical shift of C_α in the pn ternary complex (40.65 p.p.m.), like those[26] in the complexes with $[Zn(dien)]^{2+}$ and $[Zn(aepn)]^{2+}$ but unlike that with $[Zn(tren)]^{2+}$, lies well outside the range defined by the unprotonated and fully protonated (H_2pn^{2+}) forms of the ligand (39.38 and 37.76 p.p.m., respectively). The reason for this is unclear, but it does appear to be an unusual characteristic of the α-carbon atoms in aliphatic polyamines when the latter form zinc complexes which incorporate one or more six-membered rings. The second feature concerns the relative values of $K^{\mathrm{ML}}_{\mathrm{MLX}}$ for en and pn.

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* The abbreviation 2,3-tri was used for this ligand in ref. 5.

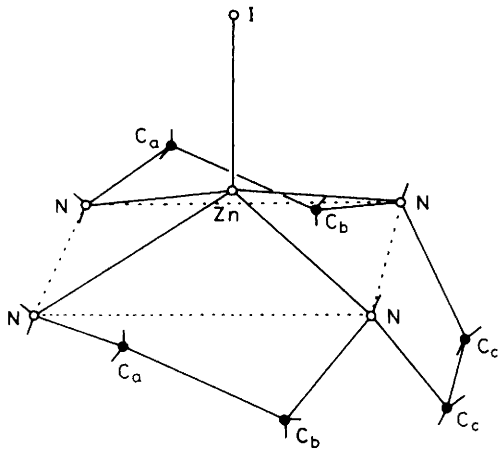

Figure 5. Structure of cation in [Zn(trien)I]I (see ref. 3)

In the complexes [ML(HA)] these ligands must bind in a unidentate fashion; as expected, the ternary stability constants $[\log K^{\mathrm{ML}}_{\mathrm{ML(HA)}} = 0.6$ and $1.6]$ reflect the respective second pK_a of en and pn (7.4 and 9.0). If the binding in the complexes [MLA] were also unidentate, the values of $\log K^{\mathrm{ML}}_{\mathrm{MLA}}$ would be expected to reflect the first pK_a of the diamine (10.2 and 10.6), but they do not. In fact, $[\mathrm{Zn(trien)(en)}]^{2+}$ is considerably more stable than $[\mathrm{Zn(trien)(pn)}]^{2+}$ ($\log K^{\mathrm{ML}}_{\mathrm{MLA}} = 2.7$ and 2.2, respectively), as would be expected if the binding were bidentate since Zn^{2+}, in common with many metal ions, tends[7] to form more stable complexes in which it is part of a five-membered chelate ring than where it is in a six-membered ring.

Only one crystal-structure determination has been reported for a trien complex of zinc, that of [Zn(trien)I]I.[3] The co-ordination around the central zinc atom is square pyramidal, with one of the iodide ions occupying the apical position and the other unco-ordinated. The zinc atom is displaced by 0.71 Å above the plane of the four N atoms of the ligand molecule, towards the iodine atom, and the Zn–N distances are all fairly long (2.13—2.21 Å).[3] The $[\mathrm{Zn(trien)}]^{2+}$ moiety has an *RS* configuration,[28] with the methylene groups of the central chelate ring eclipsed and those of the outer rings *gauche* (Figure 5). The same square-pyramidal geometry is found[29] with [Cu(trien)(SCN)]CNS and the small differences between the two structures can all be understood[3] in terms of the different ligand-field effects found in d^9 and d^{10} systems, with the latter favouring the equivalence of apical and basal bonds and the former favouring their non-equivalence. Other configurations have been reported for complexes of trien with nickel(II)[30] and cobalt(III)[31] but in these cases the well established preference of the metal for octahedral co-ordination is clearly the dominant feature. Nonetheless, there are[3] several significant similarities between analogous interatomic distances and bond angles within the M(trien) moiety in all these systems.

Probably the most striking aspect of the results (Table) is the constancy of the chemical shifts of the trien C atoms in the complexes; this is in marked contrast to the ^{13}C shifts of the ternary complexes involving zinc and certain other polyamines (*e.g.* dien and aepn) which vary[26] over several p.p.m. Treating the data as a single sample yields chemical shifts for C_a, C_b, and C_c of 39.92, 47.79, and 46.41 p.p.m., respectively, with standard deviations of 0.18, 0.19, and 0.20 p.p.m. When it is recalled that both X and trien are completely labile under the conditions used for most of this study, it is reasonable to conclude that the configuration adopted by the trien in these zinc complexes is one of considerable stability. The arrangement shown in Figure 5, with the inner co-ordination sphere of the zinc completed either by one comparatively strongly-bound unidentate ligand (as shown) or by two rather weakly-bound co-ordinating atoms (not shown), but with the structure of the trien moiety essentially as indicated in both cases, would appear from the *X*-ray evidence and from molecular models to have the necessary stability. Moreover, it would be consistent with the present ^{13}C n.m.r. results in that C_a, C_b, and C_c are all remote from X and would therefore not be expected to experience significant 'through-space' interactions with X. The present results also strengthen our previous conclusion[4] that there appears to be little transmission of inductive effect from X to the trien carbon atoms through the zinc atom, in contrast to the situation in cobalt(III) complexes.

Acknowledgements

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