Carbon-13 Nuclear Magnetic Resonance Study of the Zinc(II) Complexes of 3,7-Diazanonane-1,9-diamine and 1,2-Diaminoethane†

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Carbon-13 n.m.r. spectra are reported as a function of pH for 3,7-diazanonane-1,9-diamine (dadn), for mixtures of dadn or 1,2-diaminoethane (en) and zinc nitrate, and for mixtures of zinc and dadn with en, 1,3-diaminopropane (pn), acetate, glycine (gly), and L-alanine (ala). The pH profiles have been analysed by computer and invidual chemical shifts determined for the following species: dadn, Hdadn$^+$, H_2dadn^{2+}, H_3dadn^{3+}, H_4dadn^{4+}, [Zn(dadn)]$^{2+}$, [Zn(dadn)(OH)]$^+$, [Zn(dadn)(en)]$^{2+}$, [Zn(dadn)(pn)]$^{2+}$, [Zn(dadn)(MeCO$_2$)]$^+$, [Zn(dadn)(glyO)]$^+$, [Zn(dadn)(alaO)]$^+$, [Zn(dadn)(Hpn)]$^{3+}$, [{Zn(dadn)}$_2$(pn)]$^{4+}$, [Zn(dadn)(gly)]$^{2+}$, [Zn(dadn)(glyO)$_2$], [Zn(dadn)(ala)]$^{2+}$, [Zn(en)]$^{2+}$, [Zn(en)$_2$]$^{2+}$, and [Zn(en)$_3$]$^{2+}$. Acid dissociation constants have also been determined for the protonated dadn species and stability constants for the ternary and en complexes. Proposals are made concerning the co-ordination geometries of zinc–dadn complexes and possible generalisations are considered.

We have recently demonstrated[1–3] the feasibility of using ^{13}C chemical shifts to identify and characterise the various zinc complexes formed with organic ligands, even in rapidly exchanging equilibrium mixtures, and in the preceding paper[4] we extended this analytical application to a series of complexes formed with diethylenetriamine (dien). Our long-term objective is to see whether there might be some simple relationship between chemical shift and structure, of the type identified[5] for certain aliphatic polyamines, which would permit the separation of 'through space' (steric) and 'through bonds' (inductive) effects, and could thereby be used to build up a picture of the overall structure of a zinc complex from those of its constituent parts. In order to establish the extent to which inductive effects are transmitted from one part of the co-ordination sphere to another through the metal atom, we studied a range of complexes involving triethylenetetramine (trien)[2] or 2,2′,2″-triaminotriethylamine (tren)[3] (L) and a mono- or bi-dentate ligand, X. In both cases the evidence indicated that the structure of the L moiety obtained by *X*-ray crystal analysis with monodentate X was unchanged in solution, with the nitrogens arranged at the base of a square pyramid in the former and at the three equatorial and one of the axial positions of a trigonal bipyramid in the latter, but although a bidentate X was unable to impose an increased co-ordination number of six on the metal in [Zn(tren)X]$^{n+}$ (n = 1 or 2), it was able to do so in [Zn(trien)X]$^{n+}$.

Nonetheless, for both series of complexes the nature of X had no significant influence on the ^{13}C chemical shifts of L. In view of the contrast between this latter result and those for complexes of cobalt(III) (see, for example, refs. 6 and 7) and some other diamagnetic transition-metal ions, it was felt important to obtain confirmation, and to this end we have investigated a range of complexes involving zinc and one of the homologues of trien, 3,7-diazanonane-1,9-diamine (dadn). An additional reason for undertaking this study was to compare the effects of the different steric constraints present in the dadn and trien complexes associated with the different sizes of the central ring.

No crystal structures have been reported for zinc complexes of dadn. It has been suggested[8] on thermodynamic grounds that the co-ordination might be tetrahedral, but no mention is made[8,9] of the existence[10] of a pK_a for [Zn(dadn)]$^{2+}$ of 10.3 (which is confirmed in the present paper) and it is unclear what effect this and the presence of any 'long' zinc–ligand bonds (see below) might have had on the analysis. On the other hand, this ligand adopts a relatively strain-free configuration in the analogous copper(II) perchlorate complex[11] (with the linked five-, six-, and five-membered chelate rings in the stable *gauche*, chair, and *gauche* conformations) in which the N atoms are in the equatorial plane of an axially elongated octahedron, with oxygens in the apical positions. Moreover, it has been found[12] that nickel(II) forms an equilibrium mixture of complexes with dadn in water, of which the *trans* octahedral isomer is the dominant one, and in view of the similarity of the ionic radii of Ni^{2+}, Cu^{2+}, and Zn^{2+} in octahedral environments (0.69, 0.73, and 0.74 Å, respectively[13]), there is no obvious reason why such a configuration could not be adopted by the zinc complexes also. Such a possibility, which is supported by molecular models, appears to be strengthened by the recent report by Ito *et al.*[14] that the cyclic tetramine 1,4,8,11-tetraazacyclotetradecane (cyclam) (which is effectively dadn with its two ends joined by three linked methylene groups) forms a stable dithiocyanato complex of zinc in which the co-ordination geometry is pseudo-octahedral with the two NCS groups in the *trans* position. The alternating five- and six-membered rings are also in the *gauche* and chair conformations and the Zn^{2+} lies 0.18 Å above a plane defined by the four nitrogens of the macrocycle, while five of the Zn–N bond lengths (involving the ring and one NCS) are normal and the sixth is elongated. We undertook the present study in the hope[2,3] that the identity of the ternary complexes formed with a range of small ligands X and their chemical shifts would provide an indication of the co-ordinational preference(s) of zinc when bound to dadn.

The ^{13}C chemical shifts for aqueous solutions containing 0.22 mol dm^{-3} dadn 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 four non-equivalent carbon atoms in the following species: dadn, Hdadn$^+$, H_2dadn^{2+},

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† *Supplementary data available* (No. SUP 56689, 5 pp.): observed chemical shifts for solutions containing dadn and en. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1987, Issue 1, pp. xvii—xx.

The notation used in this paper is similar to that used previously: ligand L = dadn; ligand X = A (glyO, alaO, en, pn, or MeCO$_2^-$) or HA (gly, ala, Hpn$^+$); gly = glycine, glyO = glycinate(1−), ala = L-alanine, alaO = L-alaninate(1−), en = 1,2-diaminoethane, pn = 1,3-diaminopropane.

H_3dadn^{3+}, H_4dadn^{4+}, $[Zn(dadn)]^{2+}$, $[Zn(dadn)(OH)]^+$. Exchange between free and complexed dadn is slow on the n.m.r. time-scale at pD 7—10 but rapid above pD 10. $[Zn(dadn)]^{2+}$ dissociates below *ca.* pD 7 and it is likely that $[Zn(Hdadn)]^{3+}$ is involved here, but its characterisation was precluded by the occurrence of serious line broadening.

The pD profiles of the ^{13}C chemical shifts in solutions of Zn, dadn, and X (0.20, 0.22, and 0.20 mol dm^{-3}, respectively), where X is 1,2-diaminoethane, 1,3-diaminopropane, glycine, L-alanine, or acetic acid, are also reported. The X ligand chemical shifts have been used to compute the stability constants of the ternary complexes and the values have been compared with those obtained for the analogous trien complexes. For purposes of comparison the ^{13}C chemical shift pD profiles have been determined for solutions containing zinc (0.02 mol dm^{-3}) and en (0.05 and 0.06 mol dm^{-3}, respectively). The involvement of 'long' zinc–ligand bonds in the complexes, the singular 'zinc shifts' experienced by the carbon atoms in six-membered chelate rings, and the possible correlation between the chemical shift(s) of the X ligand in the ternary complex and its denticity are also discussed.

Experimental

The solutions were made up and the n.m.r. spectra recorded at 21 ± 1 °C as described previously;[1,5,10] pD = pH meter reading + 0.40. 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.

Results

1. *The Free Ligands.*—The C atoms in pn, alaO, and dadn are identified as shown below.

pn	$NH_2C_aH_2C_bH_2CH_2NH_2$
alaO	$C_aH_3C_bH(NH_2)CO_2^-$
dadn	$(NH_2C_aH_2C_bH_2NHC_cH_2)_2C_dH_2$

The measured chemical shifts, δ, of C_a, C_b, C_c, and C_d in dadn at different pD are represented by the solid circles in Figure 1. The solid titration curves were computed from these data by the method described in the preceding paper and ref. 10, to give the pK_a values (pK_D^c) and individual chemical shifts listed in Table 1. (The assignment of the shifts for H_4dadn^{4+} to C_b and C_c differs from that made previously.[5] Discrepancies in the pD profiles of the Zn–dadn systems assuming the original assignment led us to examine the free-ligand profile in detail between pD 6 and 8, and we now conclude that there is a single 'crossover'. The shapes of the titration curves in this region are such that the assignment actually has little affect on the derived pK_a but it would appear that the size of the cross-term needed for C_b was originally underestimated.[5]) Also given in Table 1 are the pK_a values predicted on the basis of the application of a uniform deuterium isotope effect ΔpK of 0.63[10] to the literature[9] values in H_2O (pK_H^c); in all cases the agreement is good. The four spectral lines for free dadn were consistently sharp and with relative heights (C_a:C_b:C_c:C_d) of approximately 2:2:2:1, confirming that exchange between the various protonated forms is rapid on the n.m.r. time-scale. Following previous practice, we have indicated the quality of fit of the pD profiles for the exchanging systems by the standard deviations calculated from the differences between the observed δ and those computed on the basis of the parameters listed.

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

(*a*) Chemical shifts[b]

	δ(L)	δ(HL^+)	δ(H_2L^{2+})	δ(H_3L^{3+})	δ(H_4L^{4+})
C_a	41.00	39.75	39.10	38.20	36.53
C_b	51.90	49.70	47.70	46.10	45.45
C_c	47.70	47.25	47.20	46.90	46.05
C_d	29.70	27.70	27.20	26.35	23.70

(*b*) pK_a

Measured[c]	pK_D^c	11.05	10.10	7.80	6.70
Calculated[d]	pK_D^c	10.88	10.13	7.91	6.65

[a] The 'best' values were determined from 19 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 0.088, C_b 0.063, C_c 0.065, C_d 0.088. [b] The estimated errors are ±0.1 p.p.m. [c] At 21 ± 1 °C; I various. The estimated errors are ±0.1. [d] Calculated by adding a deuterium isotope effect of 0.63 (ref. 10) to values of pK_H^c from ref. 9.

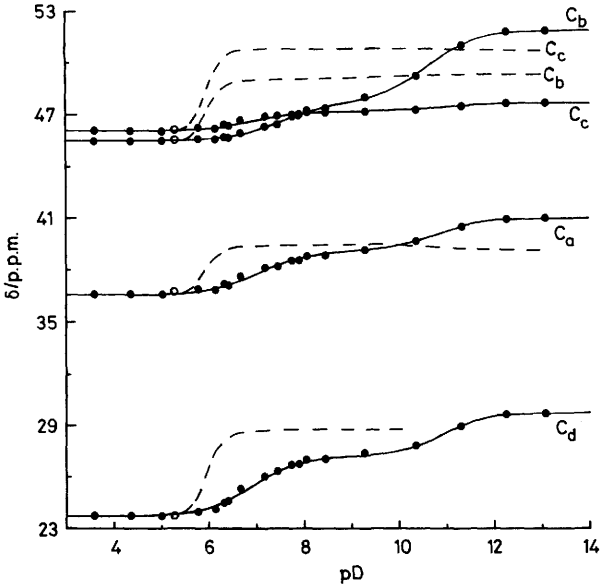

Figure 1. ^{13}C N.m.r. chemical shifts for dadn (0.20 mol dm^{-3}; ●) as a function of pD, and for $Zn(NO_3)_2$ (0.20 mol dm^{-3}) + dadn (0.22 mol dm^{-3}) at pD 5.31 (○)

2. *The Binary System.*—(*i*) Zn^{2+} + dadn. The measured chemical shifts for Zn + dadn (0.20 + 0.22 mol dm^{-3}) at different pD are given by the solid circles in Figure 2 and the open circles in Figure 1. Although the coincidence of the latter points with the respective free-ligand profiles at pD 5.31 confirms the break-up of the Zn–dadn complexes in acid solution, neither the appearance of the spectra nor the shape of the profiles above pD 6 provides unequivocal evidence about the exchange characteristics of the complexes formed. Since the analysis of the data depends on whether (as in the trien system[1]) exchange between complexes and uncomplexed ligand is rapid or whether (as with tren[3]) there is a region of slow exchange, a few additional spectra were recorded with an excess of dien > 10% to establish this point. The results are given in Table 2 and Figure 2 (open circles).

Between pD 7 and 10 the number of spectral lines indicates that in this range exchange is slow, while at high pD there are

Table 2. ^{13}C Chemical shifts (in p.p.m.) for zinc–dadn solutions (see text)

			δ(C_a)		δ(C_b)		δ(C_c)		δ(C_d)	
pD	[Zn]/ mol dm^{-3}	[dadn]/ mol dm^{-3}	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.
6.03	0.20	0.44	38.28	37.83[a]	47.10	46.96[a]	47.10	48.06[a]	26.78	25.95[a]
6.28	0.20	0.22	39.09	39.01[a]	48.67	48.55[a]	50.64	50.18[a]	28.27	28.02[a]
7.94	0.20	0.30	38.71[b]	38.68	47.11[b]	47.01	47.11[b]	47.05	26.89[b]	26.78
8.39	0.20	0.40	38.98[b]	38.92	47.56[b]	47.40	47.21[b]	47.13	27.04[b]	27.02
8.98	0.005	0.010	39.18[b]	39.22	48.01[b]	48.09	47.15[b]	47.21	27.48[b]	27.30
11.61	0.20	0.40	40.03	39.92	50.31	50.30	49.63	49.33	28.56	
13.01	0.20	0.40	40.11	40.02	50.57	50.53	49.32	49.37	28.78	
>13.1	0.20	0.40	40.03	40.02	50.50	50.53	49.37	49.37	28.70	

[a] No allowance has been made for the possible formation of $[Zn(Hdadn)]^{3+}$. [b] Peak ascribed to uncomplexed dadn; additional peaks ascribed to $[Zn(dadn)]^{2+}$ were observed at the positions indicated in Figure 2.

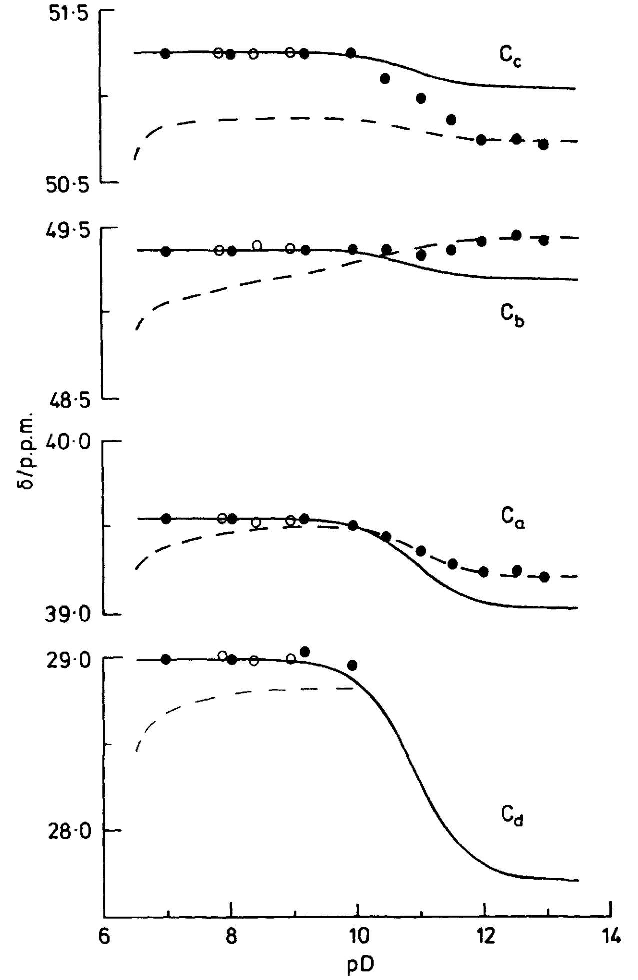

Figure 2. ^{13}C N.m.r. chemical shifts for $Zn(NO_3)_2$ (0.20 mol dm^{-3}) + dadn (0.22 mol dm^{-3}) as a function of pD (●). The concentrations used for values represented by ○ are shown in Table 2

never more than four lines, indicating that here it is rapid. The dashed lines in Figures 1 and 2 were computed by the method used for the free ligand, modified[4,10] to take account of the low- and high-pH forms of the complex {$[Zn(dadn)]^{2+}$, [ML], and $[Zn(dadn)(OH)]^{+}$, [ML(OH)], respectively; see ref. 10} and assuming rapid exchange between free and complexed ligand; the solid lines in Figure 2 assume slow exchange, except between [ML] and [ML(OH)]. The additional data used in these computations are given in Table 3. The good agreement between the computed and observed chemical shifts for all four carbons (except in the changeover regions and for C_d at high pD) confirms the exchange pattern indicated by the appearance of the additional spectra. It is thought rather more likely that this changeover to lability at around pD 10 is associated with the increase in concentration of unprotonated amino groups in free dadn (first two pK_D^c = 11.05, 10.10) than the conversion of [ML] into [ML(OH)] (pK_D^c 10.91). In support of this, the spectral lines for the 0.20 + 0.40 mol dm^{-3} solution at high pD showed markedly less broadening than for the 0.20 + 0.22 mol dm^{-3} solutions at similar pD and, whereas the concentration of free unprotonated primary amino groups will be significantly higher at the higher ratio, that of [ML(OH)] will not.

In the trien study[1] the spectral lines for the zinc-containing solutions only exhibited exchange broadening in the pD range 5—7, where the distribution diagram indicates that dissociation of $[Zn(trien)]^{2+}$ is occurring *via* the monoprotonated form $[Zn(Htrien)]^{3+}$. While line broadening was observed in this pD range with the Zn–dadn (0.20 + 0.22 mol dm^{-3}) system also (where it was unfortunately too extreme to permit chemical-shift analysis), at least one peak showed signs of it throughout the pD range studied. For C_a, C_b, and C_c the extent of line broadening was in line with the chemical-shift differences for the major species present at the pD in question, but for C_d (where the problem is exacerbated by a low relative concentration) this could not be established since it proved impossible to obtain a reliable value for δ[ML(OH)]. An attempt to obtain this directly from a dilute solution at high pD ([Zn], [dadn] = 0.005, 0.010 mol dm^{-3}, respectively; pD 12.00) failed as the spectrum was of very poor quality, while the spectra for the 0.40 + 0.20 mol dm^{-3} solution could not be used owing to the varying and uncertain contributions from bis complexes. As expected, raising the temperature led to a general sharpening of the exchange-broadened lines, but in view of the numerous equilibria involved these spectra have not been used quantitatively, nor was a kinetic line-shape analysis attempted.

(*ii*) Zn^{2+} + en. The measured chemical shifts of en in the presence of $Zn(NO_3)_2$ (0.02 mol dm^{-3}) at different pD are given by the points in Figure 3. The solid and dot-dashed lines (total [en] = 0.06 and 0.05 mol dm^{-3}, respectively) and the dotted lines were computed on the basis of the stability constants and chemical shifts listed in Table 3 and assuming the δ and pK_a values for en, Hen^{+}, and H_2en^{2+} given in ref. 10; the dashed line represents the behaviour of free en. The stability constants for $[Zn(en)_n]^{2+}$ (*n* = 1, 2, or 3) agree well with the literature values[15] and the computed curves follow the experimental points closely up to about pD 10.5 and 10.0, respectively. Above these pD values the observed chemical shift approaches that of

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

Complex		δ(dadn)				δ(X)	log K^{ML}_{MLX}
		C_a	C_b	C_c	C_d		
$[Zn(dadn)]^{2+}$	[ML]	39.56	49.35	51.25	29.00		
$[Zn(dadn)(OH)]^{+}$	[ML(OH)]	39.03	49.16	51.03			10.91[c]
$[Zn(dadn)(MeCO_2)]^{+}$	[MLA]	39.50	49.25	51.20	29.10	23.57	0.88
$[Zn(dadn)(gly)]^{2+}$	[ML(HA)]	39.80	49.30	51.25		42.72	0.78
$[Zn(dadn)(ala)]^{2+}$	[ML(HA)]	39.80	49.40	51.60		17.82 (C_a) 51.20 (C_b) 177.20 (CO_2^-)	0.85
$[Zn(dadn)(Hpn)]^{3+}$	[ML(HA)]	39.60	49.10	51.30	29.10	38.40 (C_a) 27.85 (C_b)	1.30
$[\{Zn(dadn)\}_2(pn)]^{4+}$	$[(ML)_2A]$	39.00	49.30	51.70		38.80 (C_a) 28.00 (C_b)	1.00[d]
$[Zn(dadn)(glyO)_2]$	$[MLA_2]$	40.00	49.30	50.00		45.85	0.20[e]
$[Zn(dadn)(glyO)]^{+}$	[MLA]	40.05	48.10	50.70		43.58	2.26
$[Zn(dadn)(alaO)]^{+}$	[MLA]	39.95	48.50	50.70		21.50 (C_a) 51.50 (C_b) 184.47 (CO_2^-)	1.85
$[Zn(dadn)(en)]^{2+}$	[MLA]	40.05	48.45	51.00		41.00	2.11
$[Zn(dadn)(pn)]^{2+}$	[MLA]	39.50	49.40	50.70		39.60 (C_a) 35.65 (C_b)	2.11
$[Zn(en)]^{2+}$	[MA]					41.10	6.00[f]
$[Zn(en)_2]^{2+}$	$[MA_2]$					40.50	4.95[f]
$[Zn(en)_3]^{2+}$	$[MA_3]$					40.90	2.12[f]

[a] The estimated errors are ±0.2 p.p.m. for the dadn resonances, ±0.2 p.p.m. for the en resonances in $[MA_n]$ ($n = 1$, 2, or 3), and ±0.1 p.p.m. for the X resonances except in the cases of $[(ML)_2A]$ and $[MLA_2]$, where they are ±0.3 p.p.m. The numbers of data points (in parentheses) and standard deviations for X in the ternary systems were, respectively: en (15), 0.112; pn (C_a) (12), 0.046; pn (C_b) (12), 0.17; acetate (9), 0.033; gly (1:1) (13), 0.03; gly (2:1) (10), 0.09; ala (C_a) (14), 0.055; ala (C_b) (14), 0.092; ala (CO_2^-) (6), 0.156. [b] At 21 ± 1 °C; I various. $K^{ML}_{MLX} = [Zn(dadn)X]/[Zn(dadn)][X]$ with X = $MeCO_2^-$, gly, ala, Hpn^+, glyO, alaO, en, or pn. The estimated errors in log K^{ML}_{MLA} are ±0.1 and in log $K^{ML}_{ML(HA)}$ ±0.2. [c] pK_a for $[Zn(dadn)]^{2+}$ (ref. 10). [d] $K^{ML}_{MLX} = [\{Zn(dadn)\}_2(pn)]/[Zn(dadn)(pn)][Zn(dadn)]$. Estimated error in log K^{ML}_{MLX} is ±0.4. [e] $K^{ML}_{MLX} = [Zn(dadn)(glyO)_2]/[Zn(dadn)(glyO)][glyO]$. Estimated error in log K^{ML}_{MLX} is ±0.4. [f] $K^{ML}_{MLX} = [Zn(en)_n]/[Zn(en)_{n-1}][en]$, where $n = 1$, 2, or 3. The estimated errors in log K^{ML}_{MLX} are ±0.1 for $n = 2$ and ±0.2 for $n = 1$ or 3.

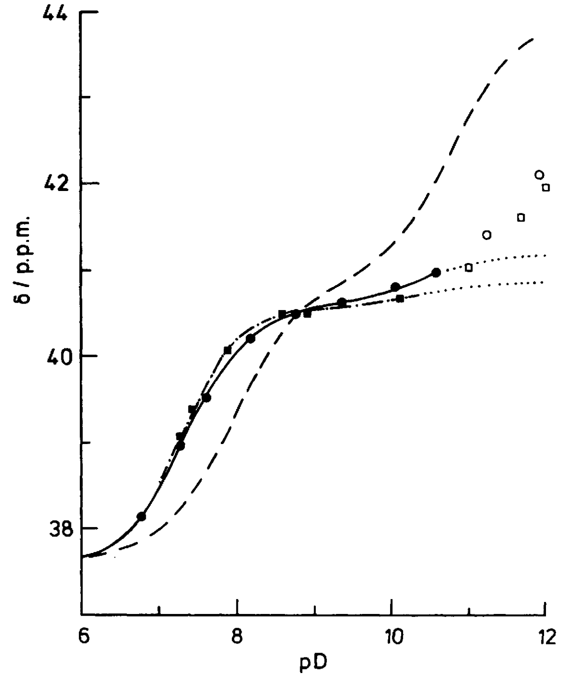

Figure 3. ^{13}C N.m.r. chemical shifts for en [0.06 (——) or 0.05 (— · — · —) mol dm^{-3}] in the presence of $Zn(NO_3)_2$ (0.02 mol dm^{-3}) as a function of pD (see text)

the free ligand, as shown by the open points in Figure 3. This deviation is attributed to the release of free ligand accompanying the precipitation of $Zn(OH)_2$ (which was observed as a fine suspension at high pD), as was found with dien (see Figure 1 of preceding paper). In support of this interpretation, the deviation occurs at a lower pD in the solution containing the lower ligand : zinc ratio because the free en is less competitive here with respect to OH^- than at the higher ratio.

3. *The* Zn^{2+} + dadn + X *Ternary Systems*.—The measured chemical shifts for the C atoms of X and dadn in mixtures of $Zn(NO_3)_2$, dadn, and X (0.20, 0.22, and 0.20 mol dm^{-3}, respectively) at different pD are given in the supplementary material (SUP 56689). The 'best fit' lines through the points were computed as before[4,10] on the basis of the formation constants K^{ML}_{MLX} and chemical shifts δ(X) listed in Table 3, and assuming the computed pD profile of free X (refs. 3 and 10, and broken lines in Figure 4). The spectral lines for X were consistently sharp and it was therefore assumed that exchange between complexed and uncomplexed forms of X was rapid throughout. Line broadening of the dadn resonances occurred as in the Zn + dadn system and for this reason it proved impossible to obtain reliable δ(C_d) values for most ternary complexes; on the basis of the appearance of additional spectra recorded with a 2:1 excess of dadn over Zn and each X (see above), the data were analysed in terms of rapid exchange between free and bound dadn except in the cases of acetate and pn below pD 10. Exchange of dadn between the various complexes was assumed to be rapid in all cases. The pD profiles for most of the ternary systems are not shown as those for X = en,

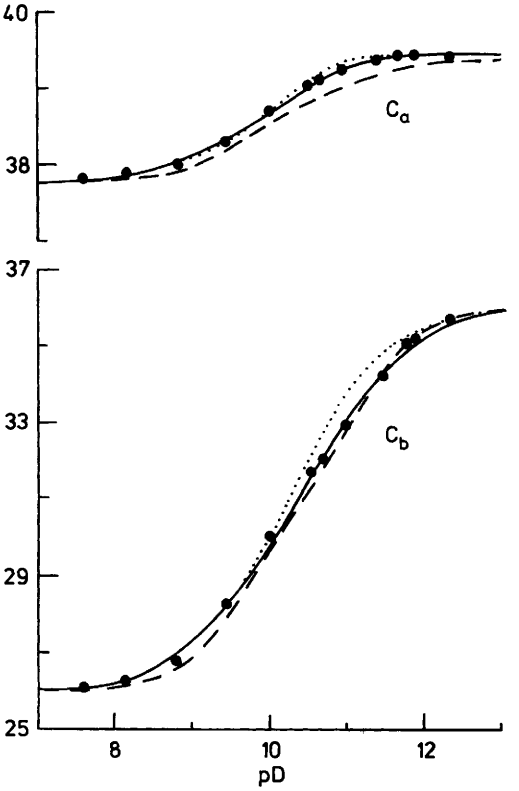

Figure 4. ^{13}C N.m.r. chemical shifts for pn in $Zn(NO_3)_2$ (0.20 mol dm^{-3}) + dadn (0.22 mol dm^{-3}) + pn (0.20 mol dm^{-3}). Dashed lines show behaviour of free ligand

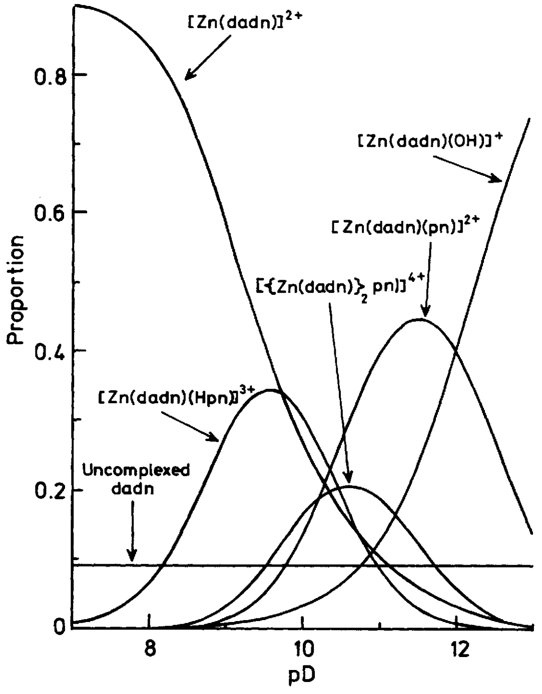

Figure 5. Distribution diagram for the various complexes and uncomplexed dadn in $Zn(NO_3)_2$ (0.20 mol dm^{-3}) + dadn (0.22 mol dm^{-3}) + pn (0.20 mol dm^{-3})

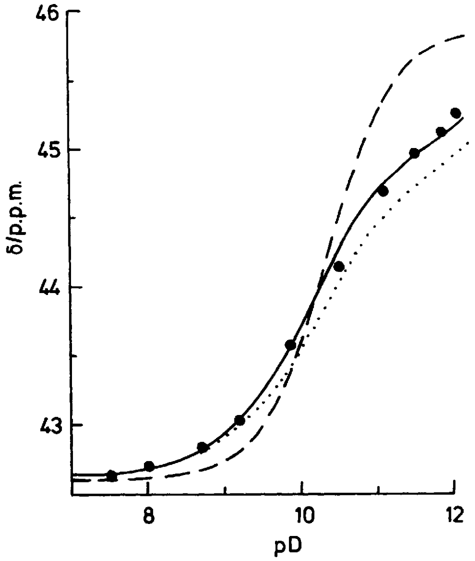

Figure 6. ^{13}C N.m.r. chemical shifts for gly (methylene C) in $Zn(NO_3)_2$ (0.20 mol dm^{-3}) + dadn (0.22 mol dm^{-3}) + gly (0.40 mol dm^{-3}). Dashed line shows behaviour of free ligand

$MeCO_2^-$, gly, and ala are similar in form to Figure 1 of ref. 2 and Figure 3 of ref. 4, and those for dadn are similar to Figure 2.

As in the Zn–trien system,[2] it was necessary to include parameters for a ternary complex formed from the monoprotonated forms of gly and ala {*i.e.* [ML(HA)]} as well as those for the unprotonated mixed complex [MLA], and failure to do so led to a significantly poorer fit to the experimental points. The data for en and acetate could be fitted satisfactorily without involving such species, while those for pn deviated significantly from the computed lines [which are shown dotted in Figure 4] in the region of pD 11 even when $[Zn(dadn)(Hpn)]^{3+}$ was included. Addition of a hydroxo ternary complex $[Zn(dadn)(pn)(OH)]^{+}$ could not produce the required deflection through the points since any contribution it might make to δ in the pD range 10.5—11.5 would necessarily increase as the pD continued to rise beyond 11.5. The involvement of a bis-ternary complex $[Zn(dadn)(pn)_2]^{2+}$, analogous to that proposed below for gly, could also be ruled out since a computer-generated pD profile showed that its range of maximum stability would be 11.5—12.5. The computed line could, however, be made to match the experimental points well (solid line, Figure 4) by including the species $[\{Zn(dadn)\}_2(pn)]^{4+}$. (Binuclear complexes are well established for zinc.[16]) A distribution diagram (in terms of dadn) for this system is shown in Figure 5.

The measured chemical shifts for the methylene C of gly in mixtures containing Zn, dadn, and gly at 0.20, 0.22, and 0.40 mol dm^{-3}, respectively, are shown by the points in Figure 6. The level of fit of the computed line (dotted) was improved (solid line) by including the bis-ternary complex $[Zn(dadn)(glyO)_2]$ in addition to [MLA] and [ML(HA)]. Similar improvements were made to the fits of the chemical-shift profiles for dadn in the same system (not shown) but in view of the very low stability constants of the bis-ternary complex the possible formation of analogous species with other X was not investigated.

Discussion

Although the stability constants of zinc complexes tend to increase[15] with the denticity of the ligand, there are exceptions to this generalisation and it is unwise to attempt to draw conclusions about the co-ordination geometries of these complexes

Table 4. Comparison of ^{13}C chemical shifts (in p.p.m.) for X ligands alone and in zinc ternary complexes

Ligand	δ(A)	δ(HA)	δ[Zn(tren)A][a]	δ[Zn(dien)A][b]	δ[Zn(dien)$_2$A][b]	δ[Zn(trien)A][c]	δ[Zn(dadn)A][d]
en	44.0[e]	40.9[e]	44.1	41.0	40.9	41.9	41.0
pn C_a	39.4[c]	38.8[c]	39.7	43.8	45.0	40.7	39.6
C_b	36.0[c]	30.8[c]	36.2	29.3	31.3	36.0	35.7
gly (CH_2)	45.9[e]	42.6[e]	45.2	43.9	43.0	44.0	43.6
ala C_a	21.5[e]	17.3[e]	21.6	21.0	20.4	21.4	21.5
C_b	52.6[e]	51.7[e]	52.0	51.0	50.4	51.8	51.5
CO_2^-	185.7[a]	176.8[a]	184.1	183.7	184.7		184.5

[a] Data from ref. 3. [b] Data from preceding paper. [c] Data from ref. 2. [d] This paper. [e] Data from ref. 10.

from their stability constants alone. Thus, for example, the successive stability constants[15] for the complexes of en (log K_f = 5.9, 5.0, and 2.0, respectively) might suggest that the third ligand molecule is bound monodentately, but Raman spectroscopy has shown[17] that there are no unbound amino groups in concentrated aqueous solutions of the tris-complex and the solution *X*-ray diffraction pattern is consistent[18] with this. In fact, the mean Zn–N distance in $[Zn(en)_3]^{2+}$(aq) (2.28 Å) is significantly longer than the 2.1 Å commonly found[19] in zinc complexes of aliphatic amines (a similar, though less pronounced, elongation has been reported[20] in the solid phase) and for this complex at least the low ΔG_f° is explicable[21] in terms of the formation of 'long' Zn–N bonds in place of the 'normal' Zn–O bonds[22] in $[Zn(OH_2)_6]^{2+}$(aq). Many recent *X*-ray structural reports, especially involving nitrogen donors, have included 'long' bonds to zinc and these could well turn out to be a common feature in the solution chemistry of this metal. Certainly, one or more 'long' bonds are implicated in the bis-ternary complex of glycine, $[Zn(dadn)(glyO)_2]$, in view of its very low stability constant (Table 3) and the low K_{MLX}^{ML} of the mono complex (if the co-ordination number of Zn does not exceed six and, as the δ values suggest, the dadn remains fully bound).

The values of K_{MLX}^{ML} are all less than 200 mol dm^{-3} and as such are much closer to those for the analogous complexes with the other tetramines, trien[2] and tren,[3] than to those with the triamine, dien.[4] (Exceptions in the latter case involve either monodentate X or additional equilibria.) This is in line with the general trend in zinc stability constants and suggests that in all the dadn [MLX] complexes the X moiety is either binding monodentately or, if bidentately, that 'long' zinc–ligand bonds are involved. The low K_{MLX}^{ML} values for monodentate HA and $MeCO_2^-$ are all close to the values for [Zn(trien)],[2] as is the value for the pn, [MLA], complex. However, the values of log K_{MLX}^{ML} for the other [MLA] complexes are *ca.* 0.6 lower and it will be argued below that these differences can be rationalised in terms of different co-ordination geometries for [ML(HA)] and [MLA] (A = $MeCO_2^-$ or pn) on the one hand and [MLA] (A = en, glyO, or alaO) on the other. The difference in log K_{MLX}^{ML} of 0.3 for [ML(Hpn)] and $[(ML)_2(pn)]$ is explicable in statistical terms if it is argued that, as seen from one end of the bridging pn, the $[Zn(dadn)]^{2+}$ moiety at the other end behaves rather like a proton. The apparent absence of a binuclear complex in the trien system may not be significant since a coincidence of chemical shifts would make its detection impossible. The same reason can be advanced for the lack of data on $[Zn(dadn)(Hen)]^{3+}$ in Table 3 since comparison with the trien system predicts that its stability constant would be very small (presumably because the proton is that much closer to the metal than in the pn complex) and its chemical shifts would in any case be expected to be close to those of $[Zn(dadn)]^{2+}$ and Hen^+.

It has been noted[2] that in some cases there appears to be an approximate correlation between the chemical shift(s) of A and its denticity in a zinc complex. For such a correlation to be of general diagnostic value it would need to be demonstrated that: (*i*) the transmission of any inductive ('through bond') effects from the other parts of the complex is minimal, *i.e.* that the Zn–A moiety can be treated as an independent fragment; (*ii*) the chemical-shift differences for the mono- and bi-dentate forms are significantly larger than any individual perturbations arising from steric ('through space') interaction with other parts of the complex (which must be presumed[23,24] to be capable of causing movement upfield or downfield); and (*iii*) the chemical shifts are unaffected (or are affected in a regular way) by whether the Zn–A bonds are 'normal' or 'long'.

Point (*i*) has already been demonstrated[1–3] for the trien and tren complexes and further evidence is provided in the present and preceding[4] papers; it seems unlikely to be invalid for the smaller ligands. To test point (*iii*), we examined in detail the pD profile of the Zn–en system in view of the evidence[18,20] for 'long' Zn–N bonds in $[Zn(en)_3]^{2+}$ and their presumed absence (*cf.* refs. 25 and 26) in the lower complexes. There is no significant difference between the δ values for mono, bis, and tris complexes (Table 3) and it therefore seems likely that the involvement of 'long' Zn–N bonds does not directly affect the chemical shift. [Unfortunately, the lower stability constants of the pn, gly, and ala complexes and/or the higher ligand pK_a values precluded the study of these Zn–A systems in a pH range where the precipitation of $Zn(OH)_2$ is always a potential problem.] Reference to Table 4, which lists δ(A) for all the zinc ternary complexes reported, together with those for the un(de-) and mono-protonated forms of the free ligand (A and HA, respectively), suggests that point (*ii*) is not a problem with en, pn, and gly although it is with the bulkier L-alanine. It is almost certain that the tren[3] complexes involve monodentate A and the two series of dien[4] complexes, bidentate A. Reflecting this difference, the chemical shifts of en, pn (C_b), and gly in the former are close to those of A, while those in the latter are much closer to δ(HA). [Although δ(C_a) in pn behaves differently from the others, it may still be used to distinguish between chelate and open-chain binding, see below.] It is also noteworthy that the δ value for gly in $[MLA_2]$ (45.9) indicates that it is monodentate, which the stability constants clearly show it to be, while for pn in $[(ML)_2A]$ the apparently contradictory indications from C_a and C_b are actually both consistent with its formulation as a binuclear complex. Thus C_b, being β to both amino groups, is even more shielded (δ 28.0) than it would be in a bidentate complex (δ *ca.* 30) while δ(C_a) confirms that this carbon is not part of a six-membered ring. Unfortunately, no clear link between δ value and denticity is discernible for any of the C atoms of L-alanine.

Comparison of the A shifts for [Zn(dadn)A] with the others in Table 4 suggests that en and glyO are both bound bidentately, as has been argued[2] for the trien analogues and their δ(A) values confirm this. On the other hand, both C atoms in the pn [MLA] complex of dadn are consistent with monodentate binding while in the trien complex the indications are mixed; δ(C_b) being typically monodentate but the rather high value of

$\delta(C_a)$ having been interpreted[2] in terms of weak chelation. In the light of the present results and of the relative stability constants, it now seems more likely that the downfield shift of pn (C_a) in $[Zn(trien)(pn)]^{2+}$ has its origin in some steric or other effect [point (*ii*) above] rather than in chelate-ring formation.

With the exception of $\delta(C_c)$, the chemical shifts of dadn in the complexes (Table 3) are in line with those reported for bidentate en, pn (C_b), and gly (Table 4) and other polyamines:[2–4] the effect of forming a zinc chelate with one of these ligands is approximately equivalent to half protonating it. It is premature to try to assess the relative contributions of the diamagnetic and paramagnetic components[23] to these 'zinc shifts' but the congruence of the δ values for A and Zn (monodentate A) suggests that the coulombic contribution is not important (*cf.* ref. 27). The unusual downfield shift of $\delta(C_c)$ appears to be a characteristic feature of the $\alpha\gamma$-carbon atoms (α to one amino group, γ to the other) in six-membered zinc–diamine rings: its occurrence in the complexes of (bidentate) pn and *N*-(2-aminoethyl)propane-1,3-diamine[2] has already been noted, and we have preliminary evidence[28] for a downfield shift with other polyamines containing the fragment $-HN(CH_2)_3NH-$. The bridging N-methylene C atom in propane-1,3-diamine-*N,N,N′,N′*-tetra-acetate (pdta) behaves in the same way[29] (δ for the tetra-anion and zinc complex are 54.5 and 60.2, respectively) and it appears that the $\alpha\gamma$-carbon in cyclam (1,4,8,11-tetra-azacyclotetradecane) does so too. In the latter complex the two N-methylene C atoms have[14] resonances at δ 47.9 and 49.4 but these are not assigned as between the carbons in the five- $[C_{(5)}]$ and the six-membered rings $[C_{(6)}]$; neither is the spectrum of the free ligand recorded. However, on the basis of the π/π^+ parameters evaluated[5] for linear polyamines, the chemical shifts for $C_{(5)}$ in the un- and fully-protonated forms of the ligand would be about 48.9 and 44.2 p.p.m., respectively, and those for $C_{(6)}$ 47.8 and 45.5 p.p.m. Repetition of the pattern observed with dadn would mean that the 47.9 p.p.m. line in the complex was $C_{(5)}$ and the 49.4 p.p.m. one $C_{(6)}$. It is also interesting to observe a large downfield shift for the $\alpha\gamma$-carbon in two analogous cyclic dioxa compounds of silicon (which, as a d^0 element, might be expected[27,29] to behave like zinc): the relevant δ values in $MePhSi[(OCH_2)_2CH_2]$ and $Ph_2Si[(OCH_2)_2CH_2]$ are,[30] respectively, 64.18 and 64.43 p.p.m. while that in the parent diol is[23] 59.2 p.p.m.

The structure of $[Zn(trien)X]^+$ (X = I) has been shown[31] to be square pyramidal, with the basal plane defined by the four N atoms and the Zn atom slightly displaced towards X, and it has been argued[2] that the same general configuration is retained in solution: tetragonal symmetry defined by the tetramine on one side of the Zn atom with either a single or two weakly co-ordinating atoms on the other. The ability of dadn to provide an N_4 donor base has been demonstrated,[11,12] while the readiness of zinc to enter a tetragonal N_4 environment is well established (see, for example, refs. 14, 32, and 33). It would appear that all the observations reported here can be rationalised in terms of two such tetragonal structures, one best described as an axially distorted *trans* octahedral complex and the other as a square pyramid in which the apical position is occupied by a bidentate ligand: the first of these would be adopted by the aqua complex [ML] and the ternaries with monodentate X {*i.e.* [ML(HA)], [ML(pn)], $[ML(glyO)_2]$, $[(ML)_2(pn)]$}, with one weakly held H_2O molecule (or glycinate ion) in the sixth (axial) position, and the second by the [MLA] complexes of en, glyO, and alaO. {Interestingly, a co-ordination change of just this type has recently been reported[34] for two zinc complexes with the N_4 macrocycle 6,7,8,13,14,15,16,17,18,19-decahydro-5*H*-dibenzo[*e,n*][1,4,8,12]tetra-azacyclopentadecine: when the anion is I^- the structure is best described as a square pyramid with the Zn atom displaced 0.41 Å from the N_4 donor plane towards the iodine in the axial site, but when it is ClO_4^- the metal lies approximately in the best plane through the N_4 donor set and is six co-ordinate overall, with perchlorates occupying the axial sites.}

It is unfortunate that no reliable δ values could be obtained for $\delta(C_d)$ in most dadn complexes, but for [MLA] (A = en, glyO, or alaO) they appeared to be in the region of 24 p.p.m. Such large upfield shifts from [ML] could be explained by the conversion of the stable chair form of the six-membered ring into the less commonly found[35] boat or twist-boat form, since such conformational changes are known[36] to be accompanied by chemical shift changes of this magnitude and direction in multi-ring organic systems. Moreover, molecular models suggest that the changes experienced by C_a, C_b, and C_c as a result of this conformational change would be minimal compared with the large movement of C_d. {An alternative formulation of [MLA] (A = en, glyO, or alaO) as a *cis* octahedral complex in which one of the primary N atoms has moved into an axial position to accommodate the second co-ordinating atom of A cannot be ruled out since the 'squashing' of the six-membered ring system could well lead to an upfield shift for C_d of about 5 p.p.m.; *cf.* ref. 29.} In addition, the fact that log K^{ML}_{MLA} (A = en, glyO, or alaO) for trien is consistently 0.5—0.6 higher than for dadn can best be explained in terms of a signficant conformational change in the dadn moiety when these [MLA] complexes are formed, the key feature presumably being the relative inflexibility of the central six-membered ring[35] compared with the five-membered ring with trien. Finally, this difference in the ease with which $[Zn(trien)]^{2+}$ and $[Zn(dadn)]^{2+}$ form ternary complexes (and therefore, presumably, bis complexes) in which the second ligand is bidentately bound would explain the different exchange characteristics of these [ML] species since it has been established[37] that an important requirement for rapid ligand–ligand exchange is the availability on the complex of a co-ordination site at which the incoming ligand can establish a foothold.

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