Zinc(II) Complexes of 4,7-Diazadecane-1,10-diamine, 4,8-Diazaundecane-1,11-diamine, and Tetraethylenepentamine: A Carbon-13 Nuclear Magnetic Resonance Study†

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

Carbon-13 n.m.r. spectra are reported as a function of pH for mixtures of zinc and 4,7-diazadecane-1,10 diamine (dadd), 4,8-diazaundecane-1,11-diamine (daud), or tetraethylenepentamine (tetren), of zinc and dadd or daud with 1,2-diaminoethane (en), 1,3-diaminopropane (pn), or glycine (gly), and of zinc and tetren with en or pn; supporting data have also been obtained from potentiometric titrations. The pH profiles have been analysed and chemical shifts determined for the following species: $[Zn(dadd)]^{2+}$, $[Zn(dadd)(en)]^{2+}$, $[Zn(dadd)(glyO)]^{+}$, $[Zn(daud)]^{2+}$, $[Zn(daud)(OH)]^{+}$, $[Zn(daud)(en)]^{2+}$, $[Zn(daud)(pn)]^{2+}$, $[Zn(daud)(glyO)]^{+}$, and $[Zn(tetren)]^{2+}$. Stability constants have been determined for the ternary complexes. The results support the proposals that $[Zn(dadd)]^{2+}$ and $[Zn(daud)]^{2+}$ contain ionizable water but $[Zn(tetren)]^{2+}$ does not.

Largely because of the d^{10} configuration of Zn^{2+}, no simple spectroscopic technique exists for determining the co-ordination geometry of zinc complexes in solution. We have recently shown[1] that it is possible to use ^{13}C n.m.r. chemical shift measurements to characterize the individual complexes formed in solutions containing zinc and an organic ligand, even when exchange is rapid on the n.m.r. time-scale, and are exploring the possibility that there might be some simple relationship between chemical shift and structure which could be used to build up a picture of the overall structure of a zinc complex from those of its constituent parts, as is now possible in certain areas of organic chemistry.[2]

In the present paper we report an investigation involving zinc and three linear polyamines: the tetramines 4,7-diazadecane-1,10-diamine (dadd; 3,2,3-tet) and 4,8-diazaundecane-1,11-diamine (daud; 3,3,3-tet) and the pentamine 3,6,9-triazaundecane-1,11-diamine (tetraethylenepentamine; tetren). Besides providing data for comparison with those from our other studies with linear polyamines,[1,3–6] it was hoped that this study would confirm proposals made by Paoletti and co-workers concerning the structures of the dadd and tetren complexes. From a comparison of the entropies and enthalpies of formation of zinc–dadd and –tetren with those for analogous complexes with other second-row metals, they had concluded that tetren forms[7] a five-co-ordinate complex containing no zinc-bound water, while zinc–dadd[8] contains one or two water molecules in addition to four Zn–N bonds. (More recently they have favoured the latter.[9] No structural conclusions were drawn in the parallel study with daud.[10]) It was our aim to decide on whether $[Zn(dadd)]^{2+}$, $[Zn(daud)]^{2+}$, and $[Zn(tetren)]^{2+}$ contain no, one, or two water molecules through the characterization of the ternary complexes formed with the potentially bidentate ligands en, pn, and gly. In our studies with triethylenetetramine (trien),[1,3] 2,2′,2″-triaminotriethylamine (tren),[11] and 3,7-diazanonane-1,9-diamine (dadn)[5] [as well as those with 3-azapentane-1,5-diamine (diethylenetriamine, dien),[4] *N*-(2-aminoethyl)propane-1,3-diamine (aepn),[6] and 4-azaheptane-1,7-diamine (dipropylenetriamine, dpt)[6]] we had found that the identities of the analogous ternary complexes formed and the values of their chemical shifts provide useful evidence about the co-ordinational preference of zinc when bound to these ligands.

The proposals of Paoletti and co-workers concerning the principal zinc complexes with dadd and tetren have been confirmed, and evidence is presented that $[Zn(daud)]^{2+}$ also contains ionizable water. Although a full structural analysis is possible for $[Zn(tetren)]^{2+}$, the ligand-exchange characteristics unfortunately preclude this for $[Zn(dadd)]^{2+}$ and $[Zn(daud)]^{2+}$.

Experimental

4,7-Diazadecane-1,10-diamine (Fluka; b.p. 103—107 °C at 0.03 Torr) and 4,8-diazaundecane-1,11-diamine (Eastman; b.p. 105 °C at 0.05 Torr) were purified by distillation. 3,6,9-Triazaundecane-1,11-diamine was isolated[7] from the commercially available amine (Aldrich) as the nitrate; the regenerated amine[7] was purified by distillation (130—135 °C at 0.05 Torr). The other chemicals were purified, and the solutions made up in D_2O as described previously;[12,13] pD = pH meter reading + 0.40. The n.m.r. spectra were recorded[12,13] at 21 ± 1 °C with a JEOL FT-100 instrument, using air-conditioning and compressed air to achieve thermostatting; additional experiments were performed on a JEOL GX-270 spectrometer. Chemical shifts were measured relative to internal 1,4-dioxane (δ 67.71) and are quoted on the δ scale; they are estimated to be reliable to ±0.12 p.p.m. when taken from a spectrum which includes a carboxylate resonance, otherwise to ±0.04 p.p.m. The potentiometric titrations were done under a CO_2-free atmosphere and the analysis of these and the n.m.r. titrations was performed as described previously.[4,12,13] Following recent practice, we have indicated the quality of fit of the pD profiles for the exchanging systems by the standard deviations calculated from the difference between the observed δ values and those computed on the basis of the parameters listed.

Results

The Free Ligands.—The C atoms in pn, dadd, daud and tetren are identified as follows:

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† *Supplementary data available* (No. SUP 56744, 7 pp.): observed and assumed chemical shifts. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1989, Issue 1, pp. xvii—xx. The notation used in this paper is similar to that used previously: L = dadd, daud, or tetren; ligand X = A(glyO, en, or pn) or HA (gly, Hen^+ or Hpn^+); gly = glycine, glyO = glycinate(1 −), en = 1,2-diaminoethane, pn = 1,3-diaminopropane.

Non-S.I. unit employed: Torr ≈ 133 Pa.

Table 1. Carbon-13 n.m.r. chemical shifts (in p.p.m.) for un- and fully protonated ligands

Ligand		C_a	C_b	C_c	C_d	C_e
dadd	(L)	39.83	33.00	47.41	48.85	
$[H_4dadd]^{4+}$	(H_4L)	37.70	24.72	46.35	44.20	
daud	(L)	39.90	32.95	47.40	47.82	29.75
$[H_4daud]^{4+}$	(H_4L)	37.77	24.75	45.85	45.73	23.63
tetren	(L)	41.09	51.92	48.78	48.80	
$[H_5tetren]^{5+}$	(H_5L)	36.45	45.75	44.25	44.25	

pn	$NH_2C_aH_2C_bH_2CH_2NH_2$
dadd	$(NH_2C_aH_2C_bH_2C_cH_2NHC_dH_2)_2$
daud	$(NH_2C_aH_2C_bH_2C_cH_2NHC_dH_2)_2C_eH_2$
tetren	$(NH_2C_aH_2C_bH_2NHC_cH_2C_dH_2)_2NH$

The pD profiles of the chemical shifts, δ, for the C atoms in en,[3] pn,[3] and gly[4,13] have already been published. The δ values for the unprotonated and fully protonated forms of dadd, daud, and tetren are given in Table 1. In each case they are the averages of at least two sets obtained from solutions in the appropriate pD region. The assignments were made as described in ref. 12 and for all three ligands were confirmed by computer fitting of the observed resonances over the whole of the relevant pD range. Details of these pD profiles will be published separately.[14] In all three cases the spectral lines were sharp throughout, with relative heights consistent with rapid exchange between the various protonated forms.

The Binary Systems.—(*i*) Zn + dadd. The comparatively high ligand pK_a values (10.70, 9.99, 8.57, and 5.86; ref. 8) mean that a considerable excess of ligand must be used to prevent the precipitation of $Zn(OH)_2$. Spectra recorded at the decimolar concentrations required for routine ^{13}C n.m.r. spectroscopy yielded only two measurable lines (corresponding to the β-carbon atoms C_b and C_d, the signals from the other two C atoms having undergone extreme exchange broadening), but complete resolution was possible at hundredth-molar concentrations in the range $8.5 < pD < 10.0$. The chemical shifts for the individual solutions are given in SUP 56744 and those for $[Zn(dadd)]^{2+}$, which are the averages of the observed values for the non-exchanging solutions, in Table 2.

The observed differential line broadening with the decimolar solutions can be understood in terms of the difference in δ between complexed and uncomplexed forms of dadd. For example, at pD 10.54 and concentrations of 0.20 (dadd) and 0.10 mol dm^{-3} (Zn), the approximate values of $|\delta_{free} - \delta_{complexed}|$ are 3.9, 1.0, 4.2, and 0.2 p.p.m., respectively, for C_a, C_b, C_c, and C_d, while the linewidths are $C_a, C_c \gg C_b > C_d$. At pD 11.67, $|\delta_{free} - \delta_{complexed}|$ for C_b increases to about 3.8 p.p.m., due to the titration of the free ligand, and this is reflected in the disappearance of the C_b line.

In their thermochemical paper on the zinc–dadd system, Barbucci *et al.*[8] reported the formation of a hydroxo complex $[Zn(dadd)(OH)]^+$ above pH 10 or so. The quality of the ^{13}C n.m.r. spectra at high pD was unfortunately not good enough to obtain chemical shifts for this species but we were able to confirm its formation potentiometrically.

Potentiometric titrations were performed on the free ligand and the binary system under similar conditions to those used for the n.m.r. study in order to provide the necessary information for the analysis of the n.m.r. data on the ternary systems. Accurate simulation of these data was not possible using the published[8] thermodynamic parameters but, as with the other tetramines trien,[1,15] dadn,[5] and tren,[11] the quality of fit was greatly improved by the introduction of parameters for weak bis complexes. Our 'best-fit' computed curves were generated using the following parameters: ligand pK_H^c (from 28 data points with standard deviation 0.012 cm^3) 10.79, 10.15, 8.68, and 5.93; complex log K_f (from 36 data points with standard deviation 0.017 cm^3); $K_f = [Zn(dadd)]/[Zn][dadd]$ or $[Zn(dadd)X]/[Zn(dadd)][X]$ with $X = H_2dadd^{2+}$, $Hdadd^+$, or dadd) 11.30 for $[Zn(dadd)]^{2+}$, 0.86 for $[Zn(dadd)(H_2dadd)]^{4+}$, 0.86 for $[Zn(dadd)(Hdadd)]^{3+}$, and 1.30 for $[Zn(dadd)_2]^{2+}$. The latter computation also incorporated a value of $\log\{K_f = [Zn(Hdadd)]/[Zn][Hdadd]\}$ of 6.0 and a pK_H^c value for $[Zn(dadd)]^{2+}$ of 11.07. Estimated errors in log K_f are ±0.4 and in the pK_a of $[Zn(dadd)]^{2+}$ ±0.3. No attempt has been made to correct for varying ionic strength as previous work[6,13] has suggested that this is unnecessary.

(*ii*) Zn + daud. This system also has high ligand pK_a values (10.61, 9.98, 8.69, and 7.35, ref. 16) and a comparatively low stability constant ($\log K_1 = 9.41$, ref. 16) and we found that $Zn(OH)_2$ was invariably precipitated below about pD 8.5. Spectra recorded using [daud] = 0.40 and [Zn] = 0.20 mol dm^{-3} showed considerable line broadening at pD < 10.5 and could not be used quantitatively; above pD 10.5 the lines became sharper as the ligand-exchange rate increased. The chemical shifts for $[Zn(daud)]^{2+}$ were determined from low concentration spectra ([daud] = 0.020, [Zn] = 0.010 mol dm^{-3}) at pD < 10.5, where ligand exchange is slow. The chemical shifts for the individual solutions are given in SUP 56744 and those for $[Zn(daud)]^{2+}$ in Table 2.

The literature reports[10,16] on the zinc–daud system make no mention of the formation of complexes other than $[Zn(daud)]^{2+}$ but recent work with similar systems[1,5,11,15] suggested that other complexes would be important in our analysis. To provide the necessary background information for the computer fitting of the 0.40 mol dm^{-3} daud + 0.20 mol dm^{-3} Zn chemical shift data (and subsequently the analysis of the daud ternary data), we performed potentiometric titrations on the daud binary system in D_2O over the pD range 8.55—12.05. The need to take account of bis complexes and a hydroxo-mono complex was confirmed and, by analogy with the dadd and trien systems, an estimated equilibrium constant for the formation of a monoprotonated-mono complex was also included in the analysis, although precipitation of $Zn(OH)_2$ meant that it was not possible to obtain direct evidence on its formation. Our 'best-fit' computed curves were generated using the following parameters: ligand pK_D^c (taken from the ^{13}C n.m.r. titration of the free ligand,[14] which involved 17 sets of data points and yielded standard deviations of 0.029, 0.060, 0.023, 0.034, and 0.071 p.p.m. for C_a, C_b, C_c, C_d, and C_e, respectively) 11.35, 10.60, 9.30, and 8.40; complex log K_f (from 39 data points with standard deviation 0.017 cm^3; $K_f = [Zn(daud)]/[Zn][daud]$, $[Zn(Hdaud)]/[Zn][Hdaud]$, or $[Zn(daud)X]/[Zn(daud)][X]$ with $X = H_3daud^{3+}$, H_2daud^{2+}, $Hdaud^+$, or daud), 9.41 for $[Zn(daud)]^{2+}$, 6.0 for $[Zn(Hdaud)]^{3+}$, 1.85 for $[Zn(daud)(H_3daud)]^{5+}$, 1.66 for $[Zn(daud)(H_2daud)]^{4+}$, 1.05 for $[Zn(daud)(Hdaud)]^{3+}$, and 11.8 for $[Zn(daud)_2]^{2+}$. Also included in the latter computation was a pK_D^c value for $[Zn(daud)]^{2+}$ of 11.33. Estimated errors in log K_f are ±0.4 and in the pK_a of $[Zn(daud)]^{2+}$ ± 0.3. Again, no attempt has been made to correct for varying ionic strength.[6,13]

In view of the large number of species formed and the restricted pD range of the rapid-exchange regime, it was only possible to obtain reliable ^{13}C chemical shifts for one additional complex, namely $[Zn(daud)(OH)]^+$ (Table 2). The other values used in the calculation of the 'best-fit' line are listed in SUP 56744.

One noteworthy feature of the stability constants for the bis complexes is that they generally increase with the number of protons involved. This suggests that in this case the protons are

Table 2. Carbon-13 chemical shifts[a] (in p.p.m.) and formation constants[b] for zinc complexes

		δ(L)							
Complex		C_a	C_b	C_c	C_d	C_e	δ(X)		log K^{ML}_{MLX}
$[Zn(dadd)]^{2+}$	[ML]	43.43	28.43	51.30	48.34				11.30[c]
$[Zn(dadd)(en)]^{2+}$	[ML(A)]	*d*	*d*	*d*	*d*			42.10	1.40
$[Zn(dadd)(glyO)]^{+}$	[ML(A)]	*d*	*d*	*d*	*d*		CH_2 CO_2^-	43.10 180.70	1.04
$[Zn(Hdadd)(en)]^{3+}$	[M(HL)A][e]	*d*	*d*	*d*	*d*			40.75	1.30
$[Zn(Hdadd)(glyO)]^{2+}$	[M(HL)A][e]	*d*	*d*	*d*	*d*		CH_2 CO_2^-	43.40 183.00	0.90
$[Zn(daud)]^{2+}$	[ML]	43.68	26.62	51.23	51.29	25.04			9.41[f]
$[Zn(daud)(OH)]^{+}$	[ML(OH)]	42.20	29.60	51.40	51.90	28.30			11.33[g]
$[Zn(daud)(en)]^{2+}$	[ML(A)]	*d*	*d*	*d*	*d*	*d*		40.00	1.88
$[Zn(daud)(pn)]^{2+}$	[ML(A)]	*d*	*d*	*d*	*d*	*d*	C_a C_b	42.50 30.90	1.26
$[Zn(daud)(glyO)]^{+}$	[ML(A)]	*d*	*d*	*d*	*d*	*d*	CH_2 CO_2^-	42.80 179.70	1.48
$[Zn(Hdaud)(en)]^{3+}$	[M(HL)A][e]	*d*	*d*	*d*	*d*	*d*		40.55	1.70
$[Zn(Hdaud)(pn)]^{3+}$	[M(HL)A][e]	*d*	*d*	*d*	*d*	*d*	C_a C_b	41.00 28.60	1.15
$[Zn(Hdaud)(glyO)]^{2+}$	[M(HL)A][e]	*d*	*d*	*d*	*d*	*d*	CH_2 CO_2^-	43.30 183.50	1.85
$[Zn(tetren)]^{2+}$	[ML]	38.63 40.55	46.16[h] 48.81[h]	45.69[h] 47.23[h]	47.43[h] 47.56[h]				

[a] The estimated errors are ±0.2 p.p.m. generally, but ±0.3 p.p.m. for tetren [ML] and ±0.4 p.p.m. for daud [ML(OH)]. The 'best' values for the ternary systems were determined from the following numbers of data points (in parentheses) with standard deviations (in p.p.m.) for X: en/dadd (8), 0.054; gly/dadd (8, CH_2), 0.078, (7, CO_2^-), 0.140; en/daud (6), 0.078; pn/daud (8), 0.083 (C_a), 0.028 (C_b); gly/daud (8, CH_2) 0.074, (6, CO_2^-) 0.190. [b] 21 ± 1 °C: *I* various. K^{ML}_{MLX} defined in text. The estimated errors (see footnote *a*) in log K^{ML}_{MLX} are ±0.2. [c] Assumed value for stability constant of $[Zn(dadd)]^{2+}$ (calculated from data in ref. 8). [d] Reliable value unobtainable. [e] Formulation uncertain. [f] Assumed value for stability constant of $[Zn(daud)]^{2+}$ (taken from ref. 16). [g] pK^c_D value for [ML]; determined potentiometrically. [h] Assignment tentative (see text).

involved in the interaction between the complexed ligand molecules and is interesting in view of the absence of any exchange broadening with the free ligand (see above) and of the increasing awareness[17] of the importance of second-sphere co-ordination. It is possible that such hydrogen-bonded interactions between the two complexed daud molecules are responsible for the observation that, in spectra containing separate complex and free-ligand resonances, the latter were generally somewhat broader than the former.

(*iii*) Zn + tetren. In the neutral and weakly alkaline regions, the ^{13}C n.m.r. spectra of solutions containing a slight excess of tetren comprise eight lines whose chemical shifts are independent of pD (Table 3). On addition of more tetren these eight peaks are retained and a further four appear, with δ values corresponding to the free ligand (predicted[14] chemical shifts for tetren at pD 8.72 are 39.9, 46.9, 45.9, and 48.0 p.p.m., respectively, for C_a, C_b, C_c, and C_d). Above about pD 10.5 there is a partial collapse of the spectral structure. Thus, the 0.055 mol dm^{-3} tetren + 0.050 mol dm^{-3} Zn solution at pD 11.45 exhibited one sharp and three broad lines, while the 0.120 mol dm^{-3} tetren + 0.060 mol dm^{-3} Zn solutions at pD 11.02 and 11.81 had three broad and four sharp lines; in each case, one of the latter was coincident with the sharp line in the pD 11.45 solution (δ 47.50) and the other three had δ values corresponding to the free ligand (predicted[14] chemical shifts for tetren C_a, C_b, C_c, and C_d are 40.8, 51.1, 48.5, and 48.5 p.p.m. at pD 11.02 and 41.0, 51.7, 48.7, and 48.7 p.p.m. at pD 11.81, respectively).

The most likely interpretation of these observations is that the eight tetren C atoms, while grouped together in four non-equivalent pairs in the free ligand, are so positioned in the complex that the members of each pair are now in different micro-environments and therefore have different chemical shifts. While $[Zn(tetren)]^{2+}$ is non-fluxional at the lower end of the pD range studied, it undergoes a partial 'loosening up' at higher pD; but complexed and free forms of the ligand are non-exchanging until very high pD (about 12.5). A detailed molecular rationalization of all this is given below. {An alternative interpretation involving an equilibrium mixture of two types of 1:1 complex is less plausible since in all spectra containing the eight pD-invariant lines the latter were all of comparable height, after allowance had been made for partial overlap. This would imply an equilibrium constant close to unity under all conditions used, which seems unlikely. Unfortunately, the complexity of the system precluded the use of either variable-temperature or correlation n.m.r. spectroscopy to obtain further evidence on this point. The stability constant of $[Zn(tetren)]^{2+}$ is very high (log K_1 > 15, ref. 18).}

The assignment of the resonances at 38.63 and 40.55 p.p.m. (Table 2) to the two C_a atoms in the complex is unambiguous since these are the only two lines lying in the protonation range of C_a for the free ligand (36.45—41.09 p.p.m., Table 1). (We have found[1,3–6,11] that the effect on a carbon atom in a polyamine of forming a zinc chelate is invariably equivalent to partially protonating it if it becomes part of a five-membered ring.) The detailed assignment of the other six lines in the complex spectrum will be made below but the pattern observed on partial collapse of the fine structure suggests what the pairing should be, if it is assumed that the width of the resulting resonance is proportional to the difference between the positions of the two original lines and that it is centred on their average δ value. Thus, the resonances at 47.43 and 47.56 p.p.m. ($\Delta\delta$ = 0.13 p.p.m.) will clearly produce the sharp line at δ 47.50, while those at 45.69 and 47.23 p.p.m. ($\Delta\delta$ = 1.54 p.p.m.) and 46.16 and 48.81 p.p.m. ($\Delta\delta$ = 2.65 p.p.m.) are the likely precursors of the broad resonances centred on about 46.5 and 47.5 p.p.m., respectively. Following this pattern, the two C_a lines ($\Delta\delta$ = 1.92 p.p.m.) would be expected to produce a broad resonance centred at about 39.6 p.p.m., as is observed. Finally, consideration of the free-ligand protonation ranges of C_b, C_c,

Table 3. Observed chemical shifts (in p.p.m.) for solutions containing tetren

		δ(L)				δ(X)	
Conditions	pD	C_a	C_b[a]	C_c[a]	C_b[a]		
b	6.57	38.59	46.16	45.65	47.38		
		40.52	48.80	47.17	47.55		
c	8.72	38.68	46.12	45.67	47.46		
		40.54	48.78	47.20	47.56		
		39.81[d]	46.90[d]	45.88[d]	48.00[d]		
b	8.94	38.63	46.16	45.67	47.46		
		40.58	48.85	47.36	47.58		
e	8.95	38.64	46.19	45.75	47.41	C_a	38.00
		40.54	48.78	47.15	47.56	C_b	26.82
f	9.10	38.65	46.16	45.67	47.48		40.73
		40.58	48.87	47.34	47.52		
e	9.93	38.57	46.17	45.73	47.40	C_a	38.57
		40.53	48.80	47.17	47.58	C_b	29.48
f	10.62	39.5[g]	47.3[g]	46.6[g]	47.46		42.02
c	11.02	39.5[g]	47.4[g]	46.6[g]	47.50		
		40.73[d]	48.53[d]	51.11[d]	48.53[d]		
e	11.10	39.4[g]	47.4[g]	46.2[g]	47.48	C_a	39.13
						C_b	32.44
b	11.45	39.7[g]	47.4[g]	46.3[g]	47.50		
c	11.81	39.7[g]	47.5[g]	46.6[g]	47.50		
		40.93[d]	48.67[d]	51.65[d]	48.67[d]		
f	12.10	39.6[g]	47.1[g]	46.66	47.56		43.85
e	12.12	39.6[g]	47.1[g]	46.70	47.64	C_a	39.56
						C_b	35.44
c	(12.49)	39.87	48.46	47.25	46.95		

[a] Assignment in complex tentative (see text). [b] [Zn] = 0.050, [tetren] = 0.055 mol dm^{-3}. [c] [Zn] = 0.060, [tetren] = 0.120 mol dm^{-3}. [d] Free-ligand peak. [e] [Zn] = 0.050, [tetren] = 0.055, [pn] = 0.050 mol dm^{-3}. [f] [Zn] = 0.050, [tetren] = 0.055, [en] = 0.050 mol dm^{-3}. [g] Broadened resonance; centre sometimes uncertain.

and C_d (Table 1) suggests that the 45.69, 47.23 p.p.m. pair is unlikely to be associated with C_b or the 46.16, 48.81 p.p.m. pair with C_d.

The Ternary Systems.—The measured chemical shifts of the ligand C atoms in the following mixtures at different pD are given in SUP 56744: Zn (0.10 mol dm^{-3}) + dadd or daud (0.20 mol dm^{-3}) + en, pn, or gly (0.10 mol dm^{-3}). Those of the ligand C atoms in the mixtures Zn + tetren + en or pn at different pD are given in Table 3.

In all cases the X resonances were consistently sharp and it was therefore assumed that exchange between complexed and uncomplexed forms of X was rapid throughout. In general, the appearances of the other ligand resonances resembled those of the same ligand in the corresponding binary system at a similar pD. Representative plots of the pD profiles for the X ligands are shown in Figure 1. The solid lines were computed using the formation constants K^{ML}_{MLX} and chemical shifts δ(X) listed in Table 2, and assuming the computed pD profiles of the free ligand (*cf.* broken lines in Figure 1) and the equilibrium constants relevant to the M + L binary system listed above. The dotted lines in Figure 1 have been constructed assuming that only [ML(A)] is formed and demonstrate the need to incorporate parameters for the monoprotonated ternary complex.

The hollow triangles and circles in Figure 1 are the experimental points for the systems Zn + dadd + pn and Zn + tetren + pn, respectively, and indicate that no detectable ternary complex formation occurs in these cases. Similarly, the δ(X) resonances for en in the presence of Zn + tetren (Table 2) are identical, to within experimental error, to those of the free en profile.[3] In view of this evidence that neither en nor gly forms a ternary complex with $[Zn(tetren)]^{2+}$, the measurements made at pD 8.95, 9.10, and 9.93 (Table 3) have been incorporated in the calculation of the average δ(L) for $[Zn(tetren)]^{2+}$ (Table 2).

Discussion

The ^{13}C n.m.r. chemical shifts of the zinc mono complexes of dadd and daud conform fully with the pattern already established[1,3–6,11] for zinc polyamine complexes. Thus, the singular downfield shifts of the five α,γ-carbons (3.6 and 3.9 p.p.m. for C_a and C_c of dadd and 3.8, 3.8, and 3.5 p.p.m. for C_a, C_c, and C_d of daud, respectively) are well in line with the negative zinc shifts we have observed for other α,γ-carbons in six-membered rings (−4.1 and −3.9 p.p.m. for C_a and C_c of dpt;[6] −3.9 and −2.9 p.p.m. for C_c and C_e of aepn[6]; and −3.3 p.p.m. for C_d of dadn[5]), and confirm that all four N atoms are co-ordinated in each case. δ(C_d) for $[Zn(dadd)]^{2+}$ is rather higher than the δ value for C_c in $[Zn(trien)]^{2+}$, another carbon in a Zn–NHR–CH_2–CH_2–NHR ring (48.34 compared with 46.40 p.p.m., ref. 1), but it is still within the range covered by the protonation of the free ligand (48.85—44.20 p.p.m.) The β-carbons in the six-membered rings of $[Zn(daud)]^{2+}$ (C_b and C_e) resonate upfield of that in $[Zn(dadd)]^{2+}$ (26.62 and 25.04, and 28.43 p.p.m., repectively), which suggests[5] that the conformations of the rings in the two complexes are different.

Unfortunately, the ligand-exchange characteristics for both zinc–dadd and zinc–daud are such that the ^{13}C n.m.r. spectra of the ternary systems provide only limited evidence about the nature of the complexes formed. 1,2-Diaminoethane and glycine both form un- and mono-protonated ternary complexes with $[Zn(dadd)]^{2+}$. The δ(A) values for [ML(A)] are consistent[5] with bidentate binding in each case but the stability constants are much lower[18] than is usual for chelation by en or

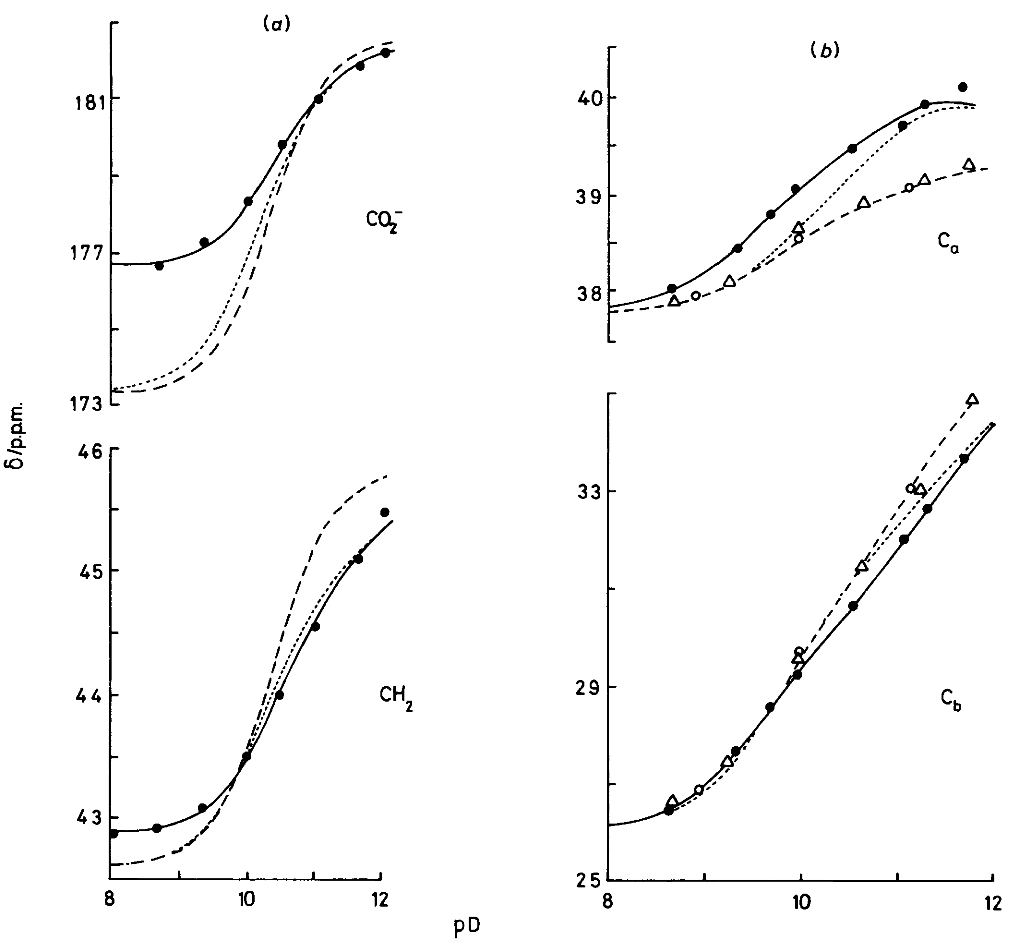

Figure 1. Carbon-13 n.m.r. chemical shifts as a function of pD for (*a*) gly in $Zn(NO_3)_2$ + dadd + gly (0.10 + 0.20 + 0.10 mol dm^{-3}) and for (*b*) pn in $Zn(NO_3)_2$ + L + pn (0.10 + 0.20 + 0.10 mol dm^{-3}), with L = daud (●) or dadd (△), or $Zn(NO_3)_2$ + tetren + pn (0.050 + 0.055 +0.050 mol dm^{-3}, ○)

glyO. A similar result for zinc–dadn was rationalized[5] in terms of the need to bring about a conformational change in the six-membered ring. The rather lower values of K^{ML}_{MLX} for dadd than dadn are consistent with the need to change the conformation of both such rings with dadd, and the lack of evidence for significant ternary complex formation with 1,3-diaminopropane is not surprising in view of the inability[5] of pn to force the conformational change on even the single ring in $[Zn(dadn)]^{2+}$. The gradual decrease in the ternary stability constants along the series trien > dadn > dadd is reflected in both the labilities of the [ML] complexes (the evidence from other labile systems being that rapid ligand–ligand exchange requires the availability in the complex of a co-ordination site at which the incoming ligand can establish a foothold[19]) and the ease with which a proton is lost from a bound water molecule (pK^c_H for complex of trien, 9.1;[13] dadn, 10.3;[13] dadd, 11.1), though not in the formation constants (log K_1 = 12.1 for trien,[18] 12.8 for dadn,[20] and 11.3 for dadd[8]).

The ligands en, pn, and gly all form un- and mono-protonated ternary complexes with $[Zn(daud)]^{2+}$. The δ(A) values indicate[5] that the [ML(A)] complexes all involve chelation of A but, as with the protonated ternary complexes of zinc–dadd, it is difficult to say whether the proton is on the A or the L ligand. The fact that the values of K^{ML}_{MLX} are all larger for $[Zn(daud)]^{2+}$ than for the corresponding complex of $[Zn(dadd)]^{2+}$ suggests that there are fewer conformational differences in the L ligand between [ML] and [ML(X)] in the case of daud than of dadd. The large changes in δ(C_b) and δ(C_d) on forming the hydroxo complex are similar to those observed with the analogous carbon (C_d) in the dadn complex[5] but they are in the opposite direction.

The complex $[Zn(tetren)]^{2+}$ is the first zinc–polyamine complex whose ^{13}C n.m.r. spectrum reveals a magnetic non-equivalence between pairs of C atoms which are equivalent in the free ligand, although this is a common feature[21] of the spectra of cobalt(III) and other non-labile complexes. This non-fluxionality of $[Zn(tetren)]^{2+}$, its non-lability, reluctance to form ternary complexes, and lack of pK_a (ref. 7) are all indicative of an unusually stable structure and the most likely one is shown in Figure 2. This is based on a trigonal bipyramid in which the equatorial positions are occupied by the two primary and the central N atoms, and incorporates the principal features of the structures of smaller zinc–polyamine complexes which have been established by *X*-ray diffraction and found[4,11,22] to be retained in solution. Thus, the two central rings are disposed along an axial edge in the same configuration (back-to-back with both rings *gauche*[23–25]) as are the two dien moieties in the meridional-octahedral ion $[Zn(dien)_2]^{2+}$, and each outer ring is positioned at a notional 120° angle relative to its neighbouring inner ring like the two five-membered rings in $[Zn(dien)(bipyam)]^{2+}$ (bipyam = di-2-pyridylamine, ref. 26) and each pair of rings in $[Zn(tren)X]^+$ (X = Cl^{27} or NCS^{28}).

Consideration of molecular models suggests that the asymmetry of the central rings with respect to the plane containing N^2, N^3, and N^4 (the vertical plane perpendicular to the paper, Figure 2) would result in different relative orientations between the pairs of methylene groups next to N^2

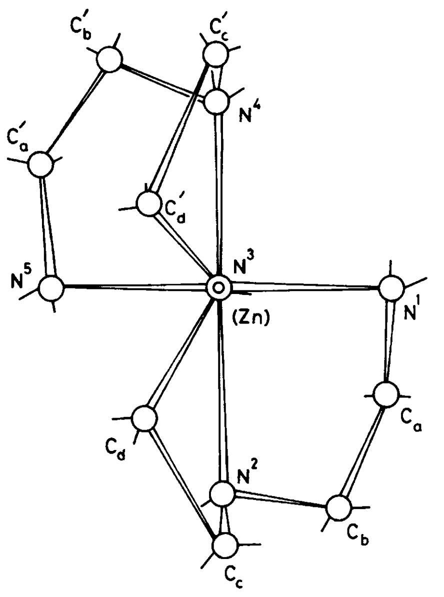

Figure 2. Proposed structure of $[Zn(tetren)]^{2+}$, viewed along the N^3–Zn axis

and N^4. This would appear to be quite sufficient to produce the observed chemical shift differences, as illustrated by the example[29] of *mer*-$[Co(dien)_2]Cl_3$. Although the two dien rings in this complex have mirror image symmetry, the two methylene carbons adjacent to the primary nitrogens are magnetically non-equivalent by virtue of the different non-bonded interactions of the primary amino groups with the NH_2 group of the other co-ordinated dien. Because the asymmetry in the zinc complex is likely to affect $\delta(C_b)$ and $\delta(C_c)$ more than $\delta(C_d)$, we have assigned the resonances at 46.16 and 48.81 p.p.m. to C_b, those at 45.69 and 47.23 p.p.m. to C_c, and those at 47.43 and 47.56 p.p.m. to C_d (see also above).

The different relative orientations between the outer pairs of rings in $[Zn(tetren)]^{2+}$ are presumably enforced through the bonding requirements of the metal ion as well as those of the ligand since it has recently been demonstrated[30] that, although considerable variability exists among the individual metal–ligand bond lengths and angles in five-co-ordinate zinc complexes, there is a very strict interdependence between them in a particular structure. In fact, consideration of the known structures suggests that that of $[Zn(tetren)]^{2+}$ is likely[30] to be somewhere between the formal trigonal-bipyramidal and square-pyramidal geometries owing to the displacement of N^1 and N^5 towards N^3 (Figure 2). This would result in an N^1ZnN^5 angle of rather more than 120° and would provide a convenient site for metal-ion attack by OH^- ions at high pH. In fact the ^{13}C n.m.r. line broadening at moderately high pD *without* an accompanying increase in the ligand–ligand exchange rate (which is at first sight surprising since inversion about N^3 would be expected to require the breaking of at least two zinc–nitrogen bonds, which would make the complex labile on the n.m.r. timescale) can be readily understood in terms of such a mechanism. As the incoming oxygen atom approaches and the co-ordination geometry at the zinc tends towards distorted octahedral, it is to be expected that a *trans*-labilizing effect would weaken the Zn–N^3 bond. The concerted breaking of this bond and the protonation of the nitrogen lone pair by a solvent water molecule would be sufficiently rapid,[31] as would the subsequent loss of its other (original) H atom to a neighbouring (solvated) OH^- ion and its re-co-ordination to the metal, to bring about inversion at N^3 on the required time-scale.

What happens above pD 12 is not entirely clear but the collapse of the ([ML] + excess of L) spectrum into four sharp resonances (pD 12.49) does indicate that ligand exchange becomes rapid. Consideration of the four δ values shows that there is at least one species present other than L and [ML] but, since this is above the range of accurate pD measurement, it was not possible to confirm its formulation as [ML(OH)].

In conclusion, we have confirmed the propositions of Paoletti and co-workers that the principal 1:1 complex of zinc with dadd contains at least one metal-bound water molecule[8] while that of tetren does not.[7] The complex $[Zn(daud)]^{2+}$ also contains ionizable water. Ternary complex formation with bidentate ligands occurs in the cases of dadd and daud but the unfavourable exchange characteristics of these complexes severely limit the structural information which can be obtained from ^{13}C chemical shifts. The complex $[Zn(tetren)]^{2+}$ does not form ternary complexes and its ^{13}C n.m.r. behaviour is consistent with a five-co-ordinate structure based on those of other zinc–polyamine complexes.

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