^{31}P nuclear magnetic resonance study of the interaction of multidentate amines with zinc(II) bis(*O,O'*-di-iso-butyldithiophosphate)

Philip G. Harrison*, Paul Brown, James McManus
Department of Chemistry, University of Nottingham, University Park, Nottingham NG7 2RD (UK)

Michael J. Hynes and Jennifer Kiely
Department of Chemistry, University College, Galway, Galway (Ireland)

(Received March 18, 1991; revised September 2, 1991)

Abstract

^{31}P NMR has been employed to study the interaction between zinc(II) bis(*O,O'*-di-iso-butyldithiophosphate), $Zn[S_2P(O^iBu)_2]_2$, and four multidentate amines (diethylenetriamine, triethylenetetramine, tetraethylenepentamine and pentaethylenehexamine) in chloroform at 294 K. The major interaction of $Zn[S_2P(O^iBu)_2]_2$ and these polyamines involves displacement of the $\{S_2P(O^iBu)_2\}$ ligands from the zinc giving $[Zn(amine)]^{2+}$ and $[S_2P(O^iBu)_2]^-$ ions in solution. The magnitudes of the equilibrium constants, K_1 ($=[\{Zn(amine)\}^{2+}][\{DDP\}^-]_2/[Zn(DDP)_2][amine]$), have been evaluated in the cases of triethylenetetramine (20.0 l mol^{-1}), tetraethylenepentamine (19.1 l mol^{-1}) and pentaethylenehexamine (1.58 l mol^{-1}). Crystalline 1:1 ionic complexes have also been isolated from these systems and characterised.

Introduction

Zinc(II) bis(*O,O'*-dialkyldithiophosphates) (ZnDDPs) have been added to motor vehicle lubricating oils for many decades as dual-function antioxidant and anti-wear agents. However, for many years very little fundamental chemical information was known about their behaviour or mode of action. Our previous studies have described solution constitution in a variety of solvents [1, 2], thermal decomposition behaviour [3, 4], and nature of interaction with small amine molecules [5, 6]. The interaction of ZnDDPs with other additives also present in the lubricating oil is a very important aspect of these materials since it may enhance function or be very deleterious. Of the many other additives present, poly(isobutenyl)succinimide polyamines (commonly derivatives of tetraethylpentamine) are present as dispersants in order to reduce carbon particulate formation, but are often mixed with ZnDDPs prior to blending with the base oil. We have previously shown crystallographically that amines bind strongly to the zinc atom of ZnDDPs, displacing the sulfur atoms of the usually-chelating DDP ligands sequentially as the denticity of the amine increases [6]. Ultimately, with tetraethylenepentamine, all DDP sulfur atoms are displaced from zinc and a cationic $[Zn(amine)]^{2+}$ species along with DDP anions are formed. In the solution phase, the ZnDDP/amine interaction behaviour is expected to be more complex with several species, including ZnDDP/amine complexes and the uncomplexed precursors, in mutual equilibrium. Since the effectiveness of each additive will be modified by the nature and strength of the binding between the individual components, it is critically important to ascertain and also quantify the equilibria which occur. For this reason we have undertaken a detailed quantitative ^{31}P NMR study of the interaction between zinc(II) bis(*O,O'*-di-iso-butyldithiophosphate), $Zn[S_2P(OiBu)_2]_2$, and four multidentate amines (diethylenetriamine, triethylenetetramine, tetraethylene-pentamine and pentaethylenehexamine) as models for polyamine dispersants.

Experimental

Synthesis of the zinc(II) bis(O,O'-dialkyldithiophosphate)–polyamine complexes

The preparation of the zinc(II) bis(*O,O'*-dialkyldithiophosphates) has been reported previously [1, 2]. Crystalline 1:1 complexes of iso-butyl ZnDDP with triethylenetetramine, tetraethylenepentamine

---

*Author to whom correspondence should be addressed.

0020-1693/91/$3.50

and pentaethylenehexamine were all obtained by the same procedure. The neat amine (1.20×10^{-3} mol) was dissolved in the minimum amount of ethanol and then added to a solution of iso-butyl ZnDDP (1.20×10^{-3} mol) also in ethanol (4 ml). The solution was allowed to stand at room temperature for several days and the crystalline product filtered. The product was recrystallised from hot ethanol, washed with pentane and dried in air. Physical and microanalytical data for the complexes are collected in Table 1. No similar crystalline product could be obtained using diethylenetriamine under identical conditions.

Infrared spectroscopy

IR spectra were recorded as KBr discs at ambient temperature using a Nicolet 20SXC Fourier transform IR spectrometer (32 scans at 2 cm^{-1} resolution).

^{31}P nuclear magnetic resonance measurements

The composite-pulse proton-decoupled ^{31}P NMR spectra of chloroform or d_1-chloroform solutions were recorded at 294 K using a Bruker WM250 Fourier transform NMR spectrometer. All samples were run using an external D_2O lock and referenced to 85% H_3PO_4 solution.

^{31}P study of the titration of the multidentate amines into a $CDCl_3$ solution of zinc(II) bis(O,O′-di-iso-butyldithiophosphate)

A solution of iso-butyl ZnDDP (*c.* 0.1 mol/l) in $CDCl_3$ was made up using volumetric glassware. The ^{31}P NMR spectrum of a 2 ml sample of the solution was recorded, and a small aliquot (1 μl) of the appropriate amine (diethylenetriamine, triethylenetetramine, tetraethylenepentamine or pentaethylenehexamine) was then added and the NMR spectrum again recorded. Further additions of amine were made and subsequent spectra recorded until additions of relatively large amounts of amine (*c.* 5 μl) produced only very small changes in the ^{31}P shift of the single resonance observed.

Computer-fitting of experimental data

The experimental data were computer-fitted using the non-linear least-squares program EQNMR [7]. Details of the derivation of the model used in the quantitative treatment of the data are shown in the Appendix. As discussed in the Appendix, values of K_1 (eqn. (A5)) cannot be determined directly using EQNMR and a consideration of the appropriate formation constants involved is required. Apart from this difference, the experimental data were fitted using the same routine as employed previously for the monomer–dimer equilibrium of zinc(II) bis(*O,O′*-dialkyldithiophosphates) in non-donor solvents [2] and subjected to the same detailed error analysis.

Results and discussion

The interaction of iso-butyl ZnDDP with multidentate polyamines affords crystalline 1:1 adducts with sharp, fairly high melting points. We have previously [6] demonstrated by X-ray crystallography that with uni, bi-, and terdentate nitrogen donor molecules zinc(II) bis(*O,O′*-dialkyldithiophosphates) form neutral complexes with five-coordinated zinc. With tetraethylenepentamine, however, ethyl ZnDDP forms the ionic complex $[Zn(TEPA)][S_2P(OEt)_2]_2$. In the present case we would, therefore, expect the isolated complexes also to be ionic in nature. The species present in solution, however, will be highly dependent upon the ZnDDP:polyamine ratio, and at low concentrations it is expected that neutral molecular complex species will be present with ionisation occurring at higher ratios.

Infrared spectra

The major features in the IR spectra of iso-butyl ZnDDP and the complexes derived from triethylenetetramine, tetraethylenepentamine and pentaethylenehexamine are listed in Table 2. Although all three complexes are proposed to contain the same *O,O′*-di-iso-butyldithiophosphate anion, the IR spec-

TABLE 1. Physical and microanalytical data for iso-butyl ZnDDP and related complexes

Compound/complex[a]	Melting point (°C)	Found (%)			Calculated (%)		
		C	H	N	C	H	N
$Zn[S_2P(O^iBu)_2]_2$	103–104	35.08	6.63		35.08	6.58	
$[Zn(TETA)]^{2+}[S_2P(O^iBu)_2]_2^-$	136–137	38.17	7.99	7.99	38.06	7.79	8.07
$[Zn(TEPA)]^{2+}[S_2P(O^iBu)_2]_2^-$	161–162	38.99	8.30	9.42	39.09	8.28	9.50
$[Zn(PEHA)]^{2+}[S_2P(O^iBu)_2]_2^-$	179–180	40.13	8.39	10.92	40.01	8.21	10.77

[a]TETA = triethylenetetramine; TEPA = tetraethylenepentamine; PEHA = pentaethylenehexamine.

tra are not identical, presumably due to crystal packing effects. Complexation has little effect on the position of the ν[(P)–O–C] band centre, but does result in the presence of shoulders at *c.* 1045 and 952 cm^{-1}. For each of the three complexes three peaks in the 777–847 cm^{-1} region arise due to ν[P–O–(C)] vibrations. Complexation causes the $\nu_{asym}(PS_2)$ absorption to increase in intensity and also to shift to higher wavenumber. For the triethylenetetramine complex two peaks are observed at 687 and 673 cm^{-1} (cf. 661 cm^{-1} for iso-butyl ZnDDP), whilst for the tetraethylenepentamine and pentaethylenehexamine complexes only single peaks are observed at 689 and 682 cm^{-1}, respectively. However, both these peaks exhibit a shoulder at lower wavenumber (679 and 674 cm^{-1}, respectively). The $\nu_{sym}(PS_2)$ absorptions of the complexes are also shifted to higher wavenumber (567–578 cm^{-1} compared to 554 cm^{-1} for iso-butyl ZnDDP). Their intensities, however, remain weak. The multiplicity of these bands serves to indicate that the two *O,O′*-di-iso-butyldithiophosphate anions in each of the complexes are crystallographically distinct as is the case for $[Zn(TEPA)][S_2P(OEt)_2]_2$ [6].

^{31}P *NMR studies*

The ^{31}P chemical shifts for chloroform solutions of the three iso-butyl ZnDDP–amine complexes isolated (108.16–111.32 ppm) are considerably higher than the chemical shift observed for iso-butyl ZnDDP (Table 3), but consistent with the range of ^{31}P chemical shifts proposed by us [1] and others [8, 9] for ionic *O,O′*-dialkyldithiophosphate.

Only a single ^{31}P resonance was observed for each of the four iso-butyl ZnDDP–amine systems studied, indicating that all phosphorus-containing species present in solution are in rapid (on the NMR time scale) dynamic equilibrium. Chemical shift versus concentration plots for the triethylenetetramine, tetraethylenepentamine and pentaethylenehexamine systems are illustrated in Figs. 1–3. In each case the addition of amine caused the ^{31}P resonance to sharpen considerably and move downfield smoothly and steadily with increasing polyamine concentration from

TABLE 3. ^{31}P chemical shifts of iso-butyl ZnDDP and related complexes in chloroform

Compound/complex	δ ^{31}P [^{1}H] (ppm)
$Zn[S_2P(O^iBu)_2]_2$	98.09^a
$[Zn(TETA)]^{2+}[S_2P(O^iBu)_2]_2^-$	108.16^b
$[Zn(TEPA)]^{2+}[S_2P(O^iBu)_2]_2^-$	110.55^a
$[Zn(PEHA)]^{2+}[S_2P(O^iBu)_2]_2^-$	111.32^a

^{a}Concentration = 0.05 mol/l. ^{b}Concentration = 0.022 mol/l.

TABLE 2. Selected IR data (cm^{-1}) for iso-butyl ZnDDP and related complexes

Compound/complex	ν[(P)–O–C]	ν[P–O–(C)]	ν_{asym} (PS$_2$)	ν_{sym} (PS$_2$)
$Zn[S_2P(O^iBu)_2]_2$	1026*, 1001s,b, 965*	857m, 823w, 796w	666*, 661m, 643*	554w
$[Zn(TETA)]^{2+}[S_2P(O^iBu)_2]_2^-$	1045*, 1020*, 1002s,b, 962*, 952*	847m, 837m, 811m	687s, 673s	567w
$[Zn(TEPA)]^{2+}[S_2P(O^iBu)_2]_2^-$	1046*, 1015*, 1001s,b, 951*	840m, 813m, 777m	689s, 679*	577w, 562w
$[Zn(PEHA)]^{2+}[S_2P(O^iBu)_2]_2^-$	1044*, 1028*, 1006s,b, 962*, 951*	842m, 807m, 786*	682s, 674*	578w, 570*

Asterisk = shoulder.

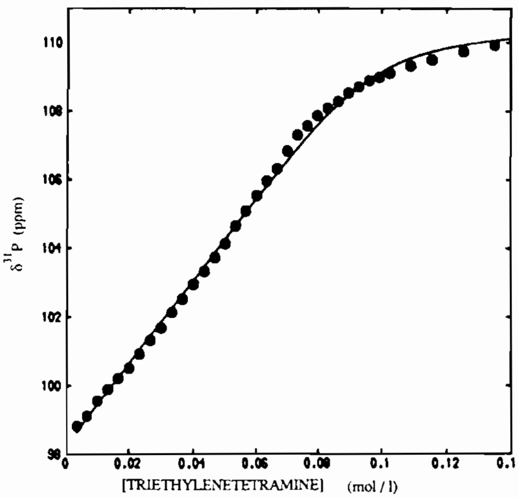


Fig. 1. Plot of ^{31}P chemical shift vs. amine concentration for the iso-butyl ZnDDP/triethylenetetramine system in chloroform.

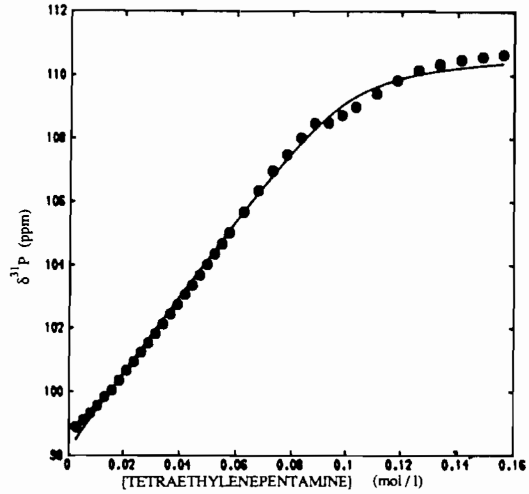


Fig. 2. Plot of ^{31}P chemical shift vs. amine concentration for the iso-butyl ZnDDP/tetraethylenepentamine system in chloroform.

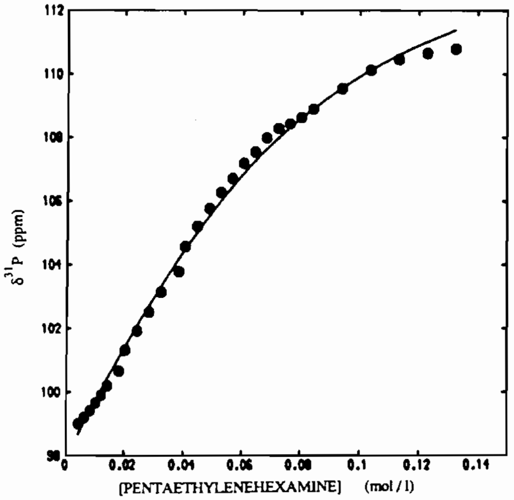


Fig. 3. Plot of ^{31}P chemical shift vs. amine concentration for the iso-butyl ZnDDP/pentaethylenehexamine system in chloroform.

c. 98.7 ppm to a maximum value of c. 110–112 ppm. The data for diethylenetriamine was similar, but could not be computer-fitted to the same model.

As detailed in the Appendix, the changes in the ^{31}P chemical shift data are interpreted in terms of the two equilibria:

$$2\mathrm{Zn(DDP)_2} \xrightleftharpoons{K} \{\mathrm{Zn(DDP)_2}\}_2 \qquad (5)$$

$$\mathrm{Zn(DDP)_2} + \mathrm{amine} \xrightleftharpoons{K_1} \{\mathrm{Zn(amine)}\}^{2+} 2\{\mathrm{DDP}\}^- \qquad (6)$$

where

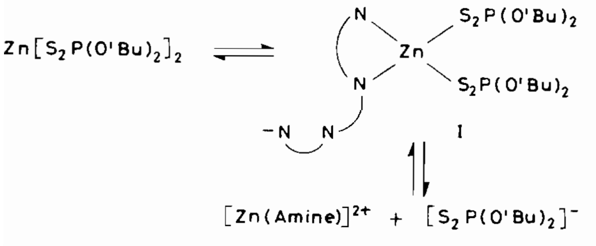
$$K = [\{\mathrm{Zn(DDP)_2}\}_2]/[\mathrm{Zn(DDP)_2}]^2 \qquad (7)$$

and

$$K_1 = [\{\mathrm{Zn(amine)}\}^{2+}][\{\mathrm{DDP}\}^-]^2/[\mathrm{Zn(DDP)_2}][\mathrm{amine}] \qquad (8)$$

Data for the iso-butyl ZnDDP/triethylenetetramine and iso-butyl ZnDDP/tetraethylenepentamine systems were found to fit this model reasonably well ($R = 1.63$ and 1.74%, respectively), indicating that the major interaction of the ZnDDP and the amine does indeed involve displacement of the DDP ligands from zinc giving $[\mathrm{Zn(amine)}]^{2+}$ and $[\mathrm{S_2P(O^iBu)_2}]^-$ ions in solution. However, close scrutiny of the calculated and experimental data in Figs. 1 and 2 shows slight discrepancies between the experimental points and the calculated fit. In both cases the experimental curve is initially somewhat shallower than the calculated curve, i.e. the increase in ^{31}P chemical shift with amine concentration is initially not as rapid as would be expected solely from the proposed model. This observation would tend to suggest that some preliminary process occurs prior to the complete displacement of the DDP ligands. This observation, however, can readily be account for by one (or both) of two processes.

(i) Initial coordination of the multidentate amine to the zinc by only one or two nitrogens occurs resulting in the formation of a neutral four-coordinated complex of the type $\mathrm{Zn[S_2P(O^iBu)_2]_2 \cdot amine(I)}$ analogous to those characterised previously [6, 9]. The formation of such a complex would also rationalise the dip in the chemical shift plots occurring at c. 108.5 ppm at a mole ratio of reactants of *c*. 1:1. Complete displacement of the DDP ligands would then occur subsequently as the remaining nitrogens coordinate to the zinc, i.e.



(ii) Sequential displacement of the two DDP ligands from zinc via an intermediate $\{\mathrm{Zn[S_2P(O^iBu)_2]_2[amine]}\}^+$ cationic species:

$$\mathrm{Zn[S_2P(O^iBu)_2]_2} \rightleftharpoons \{\mathrm{Zn[S_2P(O^iBu)_2]_2[amine]}\}^+ + [\mathrm{S_2P(O^iBu)_2}]^-$$

$$\Big\updownarrow$$

$$[\mathrm{Zn(amine)}]^{2+} + [\mathrm{S_2P(O^iBu)_2}]^-$$

Both of these processes would account for the observed chemical shift trends. However, at present we are unable to refine the data further including either of these two possibilities, and hence no distinction may be made as to their contribution to the equilibria.

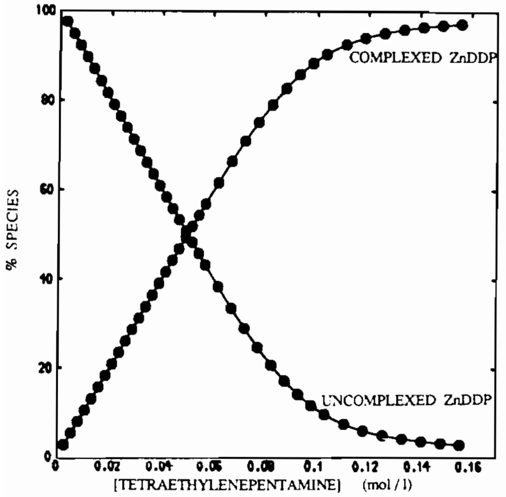


Fig. 4. Species distribution plot for the iso-butyl ZnDDP/tetraethylenepentamine system in chloroform.

The fit obtained for the pentaethylenehexamine system is also acceptably good ($R = 2.48\%$) (Fig. 3), although not as good as the other two. One possible explanation for the poorer fit in this case is that as a hexadentate ligand it is conceivable that the ligand could coordinate to more than one zinc centre, resulting in the formation of complexes other than the species included in the model.

It proved impossible to fit the data obtained for the diethylenetriamine system to the proposed model. In this case it is highly probable that, because the ligand only contains three nitrogen donor sites, a more stable neutral complex analogous to the $\mathrm{Zn[S_2P(O^iPr)_2]_2 \cdot ter}$ (ter = terpyridine) complex [6] is formed initially. Since further displacement of the DDP ligand would involve a second triamine molecule; the second stage would be expected to be significantly slower than for the higher polyamines. That complete displacement of the DDP ligands from zinc does occur even in this case is apparent from the high chemical shifts (> 110 ppm) observed at triamine:Zn ratios of $\geqslant \sim 2$.

Calculated values for the equilibrium constants, K_1, for the complexation of triethylenetetramine, tetraethylenepentamine and pentaethylenehexamine with iso-butyl ZnDDP in chloroform are shown in Table 4. The values of the triethylenetetramine and tetraethylenepentamine complexes are very similar (20.0 and 19.1 l mol^{-1}, respectively). The value for the pentaethylenehexamine complex is, however, considerably lower (1.58 l mol^{-1}). It is also interesting to note that the calculated values for the $[\mathrm{S_2P(O^iBu)_2}]^-$ anion for the tetramine and pentamine systems are also very similar (110.6 and 110.8 ppm, respectively), whilst the value for the hexamine system is somewhat higher (115.7 ppm) (see footnote to Table 4).

TABLE 4. Calculated values for equilibrium constants (K_1) and chemical shifts (δ_4) for the interaction of iso-butyl ZnDDP with polyamines in $CDCl_3$

Amine ligand	Equilibrium constant (K_1) (l mol^{-1})	δ ^{31}P dissociated DDP ligand (δ_4) (ppm)	R^a	No. of data points
Triethylenetetramine	20.0	110.6	1.63	36
Tetraethylenepentamine	19.1	110.8	1.74	38
Pentaethylenehexamine	1.58	[115.7]^b	2.48	29

[a] $R = \left[\left(\dfrac{\Sigma w_i(\delta_{calc} - \delta_{obs})^2}{\Sigma w_i \delta_{obs}}\right)\right]^{1/2}$. [b] High value due to poor fit at high chemical shift values.

The species distribution plot for the pentamine system is shown in Fig. 4. From this it can be seen that at a amine:Zn ratio of ~1 formation of the ionic complex occurs to an extent of *c.* 90% rising to *c.* 98% at a ratio of *c.* 1.5.

Acknowledgements

We thank the SERC and the ESSO Petroleum Company Ltd. for support in the form of a CASE Award (to P.B.), and E.O.L.A.S. for a studentship (to J.K.).

References

1 P. G. Harrison and T. Kikabhai, *J. Chem. Soc., Dalton.*, (1987) 807.
2 P. G. Harrison, P. Brown, M. J. Hynes, J. M. Kiely and J. McManus, *J. Chem. Res.*, *S*(1991) 165; *M* (1991) 1771.
3 P. G. Harrison and T. Kikabhai, *Wear, 116* (1986) 25.
4 P. G. Harrison and P. Brown, *Wear, 148* (1991) 123.
5 P. G. Harrison, M. J. Begley, T. Kikabhai and F. Killer, *J. Chem. Soc., Dalton Trans.*, (1986) 925.
6 P. G. Harrison, M. J. Begley, T. Kikabhai and F. Killer, *J. Chem. Soc., Dalton Trans.*, (1986) 929.
7 D. Cunningham, M. J. Hynes and J. McManus, *J. Organomet. Chem.*, in press.
8 C. Glidewell, *Inorg. Chim. Acta, 25* (1977) 159.
9 M. G. B. Drew, M. Hasan, R. J. Hobson and D. A. Rice, *J. Chem. Soc., Dalton Trans.*, (1986) 1161.

Appendix

Derivation of the model used to describe ZnDDP–amine interactions in solution

In the general case of species with NMR active nuclei in rapid (on the NMR time scale) dynamic equilibrium:

$$m\mathrm{M}+n\mathrm{L} \rightleftharpoons \mathrm{M}_m\mathrm{L}_n \qquad \text{(A1)}$$

the chemical shift of the observed single resonance, δ_{obs}, will be given by the weighted mean of the contributing species, i.e.:

$$\delta_{\mathrm{obs}}=\sum_{\substack{m=1\\n=0}}^{\substack{m=i\\n=j}} \delta_{mn}m[\mathrm{M}_m\mathrm{L}_n]/[\mathrm{M}]_0 \qquad \text{(A2)}$$

where δ_{mn} = chemical shift of the metal–ligand complex, m = number of metal atoms present in the complex, n = number of ligands in the complex, $[\mathrm{M}_m\mathrm{L}_n]$ = concentration of metal–ligand complex, $[\mathrm{M}]_0$ = initial total concentration of metal, i and j are the maximum values of m and n, respectively.

$$\text{Since } [\mathrm{M}_m\mathrm{L}_n]=\beta_{mn}[\mathrm{M}]^m[\mathrm{L}]^n \qquad \text{(A3)}$$

where β_{mn} = formation constant for $\mathrm{M}_m\mathrm{L}_n$, [M] = concentration of metal, [L] = concentration of ligand, then eqn. (A2) is transformed into

$$\delta_{\mathrm{obs}}=\sum_{\substack{m=1\\n=0}}^{\substack{m=i\\n=j}} \delta_{mn}\beta_{mn}m[\mathrm{M}]^m[\mathrm{L}]^n/[\mathrm{M}]_0 \qquad \text{(A4)}$$

In the specific case of the interaction of polyamines with ZnDDPs, the overall equilibria may be expressed by eqns. (A5) and (A7):

$$2\mathrm{Zn(DDP)_2} \overset{K}{\rightleftharpoons} \{\mathrm{Zn(DDP)_2}\}_2 \qquad \text{(A5)}$$

$$\mathrm{Zn(DDP)_2}+\mathrm{Amine} \overset{K_1}{\rightleftharpoons} \{\mathrm{Zn(Amine)}\}^{2+}2\{\mathrm{DDP}\}^- \qquad \text{(A6)}$$

where

$$K=[\{\mathrm{Zn(DDP)_2}\}_2]/[\mathrm{Zn(DDP)_2}]^2 \qquad \text{(A7)}$$

and

$$K_1=[\{\mathrm{Zn(Amine)}\}^{2+}][\{\mathrm{DDP}\}^-]^2/[\mathrm{Zn(DDP)_2}][\mathrm{amine}] \qquad \text{(A8)}$$

Thus the observed chemical shift, δ_{obs}, can be expressed by:

$$\delta_{\mathrm{obs}}=([\mathrm{Zn(DDP)_2}]\delta_1+[\{\mathrm{Zn(DDP)_2}\}_2]\delta_1+[\{\mathrm{Zn(DDP)_2}\}_2]\delta_3 + [\{\mathrm{Zn(amine)}\}^{2+}\{\mathrm{DDP}\}_2{}^-]\delta_4)/[\mathrm{Zn(DDP)_2}]_0 \qquad \text{(A9)}$$

where $\delta_1 = {}^{31}\mathrm{P}$ chemical shift of chelating DDP in free monomer or dimer, $\delta_3 = {}^{31}\mathrm{P}$ chemical shift of bridging DDP in free dimer, $\delta_4 = {}^{31}\mathrm{P}$ chemical shift of dissociated ionic DDP^-, $[\mathrm{Zn(DDP)_2}]_0$ = initial total concentration of monomer. Defining the formation constants β, β_2, and β_3 according to eqns. (A10), (A11) and (A12):

$$2\mathrm{Zn}+4\mathrm{DDP} \overset{\beta}{\rightleftharpoons} \{\mathrm{Zn(DDP)_2}\}_2$$

$$\beta=[\{\mathrm{Zn(DDP)_2}\}_2]/[\mathrm{Zn}]^2[\mathrm{DDP}]^4 \qquad \text{(A10)}$$

$$\mathrm{Zn}+2\mathrm{DDP} \overset{\beta_2}{\rightleftharpoons} \mathrm{Zn(DDP)_2}$$

$$\beta_2=[\mathrm{Zn(DDP)_2}]/[\mathrm{Zn}][\mathrm{DDP}]^2 \qquad \text{(A11)}$$

$$\mathrm{Zn}+\mathrm{amine} \overset{\beta_3}{\rightleftharpoons} \mathrm{Zn(amine)}$$

$$\beta_3=[\mathrm{Zn(amine)}]/[\mathrm{Zn}][\mathrm{amine}] \qquad \text{(A12)}$$

the expression for δ_{obs} may be rewritten as

$$\delta_{obs} = ([Zn][DDP]^2\beta_2\delta_1 + [Zn]^2[DDP]^4\beta\delta_1 + [Zn]^2[DDP]^4\beta\delta_3 + [Zn][amine]\beta_3\delta_4)/[Zn(DDP)_2]_0 \tag{A13}$$

Since a value for β_2 is not available, a value sufficiently high (10^{10}) is assumed so that, at the concentrations of the ZnDDP monomer used, all the Zn and DDP are complexed (i.e. there is no free DDP). The value of the association constant, K, for iso-butyl ZnDDP in $CHCl_3$ has been determined previously by us [2] ($K = 7.37$ l mol^{-1}), and it is possible to express β in terms of β_2 and K via eqns. (A8) and (A10) giving

$$\beta = K[Zn(DDP)_2]^2/[Zn]^2[DDP]^4 \tag{A14}$$

but since from eqn. (A12)

$$[Zn(DDP)_2] = \beta_2[Zn][DDP]^2 \tag{A15}$$

thus it follows that $\beta = \beta_2^2$ (A16)

which enables a value to be deduced for β from the previously determined value of K and the assumed value of β_2. Values of β_3 and δ_4 may then be refined using EQNMR, and K_1 can be calculated from the values obtained for β_3 via eqns. (A11) and (A12). Substitution for [Zn(amine)] and $[Zn(DDP)_2]$ into eqn. (6) reveals that

$$K_1 = \beta_3/\beta_2 \tag{A17}$$

i.e. K_1 is calculated from the refined value of β_3 and the assumed value of β_2. An important point to note is that if the value of β_2 is increased by an arbitrary factor then β_3 will also be increased by the same factor so that K_1 remains independent of the value chosen for β_2.