Proton and Phosphorus-31 Nuclear Magnetic Resonance Study of Zinc(II) *O,O'*-Dialkyl Dithiophosphates in Solution

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Proton and ^{31}P n.m.r. have been employed to investigate the constitution and behaviour of zinc(II) *O,O'*-dialkyl dithiophosphates in solution. The complexes $Zn[S_2P(OR)_2]_2$ (R = Et or Pr^i) are principally dimeric in chloroform and toluene with dissociation constants, K_D (R, solvent), to monomers of 1.81×10^{-2} (Et, $CDCl_3$), 3.08×10^{-2} (Et, toluene), 4.45×10^{-2} (Pr^i, $CHCl_3$), and 7.17×10^{-2} mol l^{-1} (Pr^i, toluene) at 29 °C. Higher ^{31}P chemical shift values and conductance data for solutions of these compounds in ethanol and tetrahydrofuran indicate that co-ordination of solvent and ligand ionization occur in these solvents. The ^{31}P chemical shifts for complexes $Zn[S_2P(OR)_2]_2 \cdot L$ increase in the order L = pyridine < 2,2'-bipyridine < 2,2':6',2"-terpyridine, and comparison with known structural data has shown that this change is due primarily to an opening of the SPS bond angle of the $S_2P(OR)_2$ ligands. The 'basic' zinc(II) *O,O'*-dialkyl dithiophosphates, $Zn_4[S_2P(OR)_2]_6O$, are unstable in solution, spontaneously, though reversibly, decomposing to 'normal' $Zn[S_2P(OR)_2]_2$ and zinc(II) oxide as the temperature is increased. Pyridine (py) causes an irreversible decomposition of $Zn_4[S_2P(OR)_2]_6O$ to $Zn[S_2P(OR)_2]_2 \cdot py$ and zinc(II).

Zinc(II) bis(*O,O'*-dialkyl dithiophosphates), $Zn[S_2P(OR)_2]_2$, often referred to as 'normal' zinc *O,O'*-dialkyl dithiophosphates, have been employed as additives to motor vehicle lubricating oils for over four decades owing to the efficacy of their dual function as both antioxidant and antiwear agents. In contrast, their primary hydrolysis products, the so-called 'basic' cluster compounds of composition $Zn_4[S_2P(OR)_2]_6O$, exhibit much lower activity in both respects, and are regarded as undesirable in lubricating oil additive packages. Although the mode of operation of these additives has been investigated widely[1–6] there is a paucity of information regarding their interaction with other additives such as detergents and dispersants. Such interactions are of importance since they may have a profound reciprocal effect on the performance of each.[7–10] In this paper, we report ^{1}H and ^{31}P n.m.r. studies of the solution behaviour of both 'normal' and 'basic' zinc *O,O'*-dialkyl dithiophosphates, their interconversion, and their interaction with a variety of nitrogen-donor molecules (as models for dispersant additives and their degradation products).

Experimental

The synthesis and characterisation of the *O,O'*-dialkyl dithiophosphato–zinc(II) compounds has been reported previously.[11,12] ^{1}H N.m.r. data were obtained using a Bruker WM250 spectrometer operating at 29 °C. ^{31}P N.m.r. data were obtained employing either a Bruker WM250 spectrometer operating at 29 °C with an external D_2O lock, or a JEOL FX90Q instrument operating at 27 °C with an external $CDCl_3$ lock. ^{31}P Chemical shifts are quoted with reference to 85% H_3PO_4; shifts to high frequency are positive in sign. Computer fitting of the ^{31}P chemical shift data in terms of solution equilibria is similar to that reported previously.[13] Theoretical details are given in the Appendix.

Results and Discussion

The Constitution of Solutions of Zinc(II) *Bis*(O,O'*-dialkyl dithiophosphates*).—Solid-state structural data are available for two zinc(II) bis(*O,O'*-dialkyl dithiophosphates). The *O,O'*-diethyl derivative exhibits a one-dimensional polymeric structure in which one $S_2P(OEt)_2$ ligand chelates each zinc, whilst the second bridges zinc atoms in the chain.[14] The *O,O'*-diisopropyl homologue has a dimeric rather than a polymeric structure, but again each zinc is chelated by one $S_2P(OPr^i)_2$ ligand and the two zinc atoms of the dimer unit bridged by the other $S_2P(OPr^i)_2$ groups.[15] The chelation and bridging is essentially symmetrical and very similar for both compounds, and in each the zinc atoms have a distorted tetrahedral co-ordination polyhedron. No data have been reported for higher homologues.

Data concerning the solution constitution and molecularity are, however, sparse. A rather old study by Heilweil[16] employing vapour-pressure osmometry indicated that solutions of $Zn[S_2P(OPr^i)_2]_2$ in benzene comprise an equilibrium mixture of dimeric and monomeric molecules. Tendency towards association into dimers decreased with increasing chain length for higher homologues, and no association was found to occur for the C_{18} derivative. In cyclohexane solution, the Pr^i derivative appeared to exist primarily as a trimer species.

Both the ^{1}H and ^{31}P n.m.r. spectra of solutions of $Zn[S_2P(OR)_2]_2$ (R = Et or Pr^i) exhibit only one set of resonances due to the *O,O'*-dialkyl dithiophosphato ligands, *i.e.* all types of ligand present in solution are in rapid dynamic equilibrium on the n.m.r. time-scale affording a time-averaged spectrum. The presence of two triplet methyl group resonances and two quartet methylene group resonances in the ^{1}H n.m.r. spectrum of $Zn[S_2P(OEt)_2]_2$ [Figure 1(*a*)] is due to three- and four-bond proton coupling to phosphorus. Three-bond coupling of the methine proton of the Pr^i group to phosphorus is also observed in $Zn[S_2P(OPr^i)_2]_2$, but not four-bond coupling. However, in this compound, the magnitude of the three-bond ^3J(P–H) coupling constant is fortuitously twice that of the three-bond ^3J(H–H) coupling, resulting in the observation of a pseudo-nonet, rather than two septets, for the methine protons (Table 1).

The ^{31}P chemical shift is dependent upon the nature of the alkyl group, solvent, and concentration, and data are given in Table 2 and illustrated in Figure 2. In the non-donor solvents $CDCl_3$ and toluene, the ^{31}P chemical shifts of both the Et and Pr^i derivatives decrease steadily and smoothly with decreasing concentration. The chemical shifts for the Pr^i derivative are lower than those of the Et derivative for the same concentration range, reflecting transmission of the inductive effect of the

Table 1. ^{1}H N.m.r. data for $CDCl_3$ solutions of $Zn[S_2P(OR)]_2$, $Zn_4[S_2P(OR)_2]_6O$ (R = Et or Pr^i), and $Zn_4[S_2P(OEt)_2]_6S$

	$Zn[S_2P(OEt)_2]_2$	$Zn_4[S_2P(OEt)_2]_6O$ [a]	$Zn_4[S_2P(OEt)_2]_6S$ [a]	$Zn[S_2P(OPr^i)_2]_2$	$Zn_4[S_2P(OPr^i)_2]_6O$ [b]
$\delta(CH_3)^c$/p.p.m.	~1.4(3)	1.34(3)	1.36(3)	~1.41(2)	1.34(2)
$\delta(CH_2)^c$/p.p.m.	~4.3(4)	~4.1(4)	~4.2		
$\delta(CH)^c$/p.p.m.				~4.9 [d]	~4.8 [d]
$^3J(^1H-^1H)$/Hz	7.1	7.0	7.0	6.3	6.2
$^3J(^{31}P-^1H)$/Hz	9.7	9.2	~9.0	~12.6	~12.6
$^4J(^{31}P-^1H)$/Hz	0.6				

[a] Spectrum also contains resonances due to $Zn[S_2P(OEt)_2]_2$ (see text). [b] Spectrum also contains resonances due to $Zn[S_2P(OPr^i)_2]_2$ (see text). [c] Multiplicities in parentheses. [d] Pseudo-nonet.

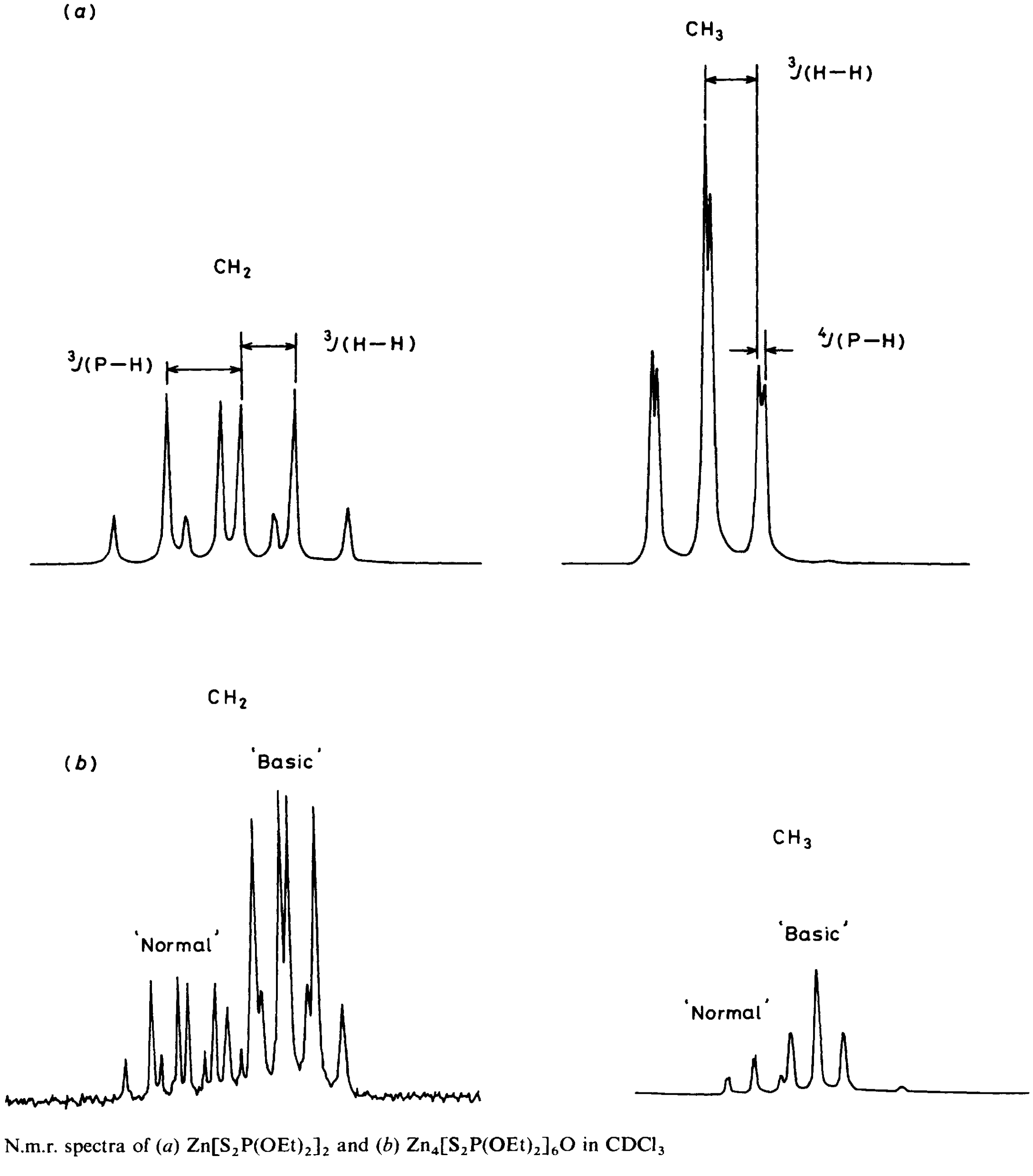


Figure 1. ^{1}H N.m.r. spectra of (*a*) $Zn[S_2P(OEt)_2]_2$ and (*b*) $Zn_4[S_2P(OEt)_2]_6O$ in $CDCl_3$

additional methyl group through to the phosphorus centre. These changes of chemical shift with concentration we ascribe to the presence of an equilibrium involving a dimeric species (**I**), possessing a bridged structure similar to that found in the solid state for the Pr^i derivative,[15] and a chelated monomeric species (**II**). Computer fitting of the chemical shift data in these solvents to this model afforded the calculated dissociation constants, K_D, and the chemical shift values for the bridged and chelated $S_2P(OR)_2$ ligands, δ_b and δ_c, respectively, listed in Table 3. The dashed lines in Figure 2 represent calculated values. Experimentally observed chemical shift values fall in the general range (87—101 p.p.m.) proposed by Glidewell[17] for chelating or

Table 2. Concentration dependence of the ^{31}P chemical shift of solutions of zinc(II) *O,O*-dialkyl dithiophosphates in various solvents

$Zn[S_2P(OEt)_2]_2$–$CDCl_3$

Concn.[a]	$\delta(^{31}P)$[b]	Residuals ($\times 10^2$)
499	98.3	−0.6
399	98.1	−0.3
319	97.9	0.01
256	97.7	1.0
204	97.5	2.1
164	97.35	−0.4
131	97.2	−2.2
105	97.0	2.4
84	96.9	−1.8
67	96.8	−4.7
54	96.6	4.4

$Zn[S_2P(OEt)_2]_2$–$C_6H_5CH_3$

Concn.[a]	$\delta(^{31}P)$[c]	Residuals ($\times 10^3$)
498	97.07	−8.4
398	96.80	0.6
319	96.54	12.0
255	96.32	−6.0
204	96.07	2.2
163	95.89	−3.6
131	95.71	−5.2
104	95.57	−36.0
84	95.39	3.9
67	95.24	25.0
53	95.16	−8.9
43	95.06	4.6

$Zn[S_2P(OEt)_2]_2$–thf

Concn.[d]	$\delta(^{31}P)$[c]
999	99.48
799	99.56
639	99.70
512	99.90
409	99.89
327	99.99
262	100.07
210	100.07
168[a]	100.09
134[a]	100.13
107[a]	100.17
86[a]	100.21

$Zn[S_2P(OPr^i)_2]_2$–$CHCl_3$

Concn.[a]	$\delta(^{31}P)$[c]	Residuals ($\times 10^3$)
500	93.09	1.7
400	92.95	2.3
320	92.83	−8.7
256	92.70	−0.06
205	92.58	9.8
164	92.50	−1.0
131	92.40	1.8
105	92.32	5.6
84	92.26	−0.7
67	92.20	2.1
54	92.16	−4.1

$Zn[S_2P(OPr^i)_2]_2$–$C_6H_5CH_3$

Concn.[a]	$\delta(^{31}P)$[b]	Residuals ($\times 10^2$)
500	94.62	5.6
400	94.42	−3.9
320	94.27	−16.0
256	93.72	15.0
205	93.65	1.0
164	93.47	0.5
131	93.36	−4.6
105	93.19	−1.0
84	93.00	6.5
67	92.97	−0.18
54	92.90	−0.87
43	92.85	−2.6

$Zn[S_2P(OEt)_2]_2$–C_2H_5OH

Concn.[d]	$\delta(^{31}P)$[c]
998	101.26
798	101.26
638	101.28
511	101.28
409	101.30
327	101.30
262	101.30
209	103.32
167	101.34
134[a]	101.34
107[a]	101.36
86[a]	101.36
69[a]	101.38

[a] Concentration of dimer (mol l^{-1} × 10^3). [b] Bruker WM250 instrument. [c] JEOL FX90Q instrument. [d] Concentration of monomer (mol l^{-1} × 10^3).

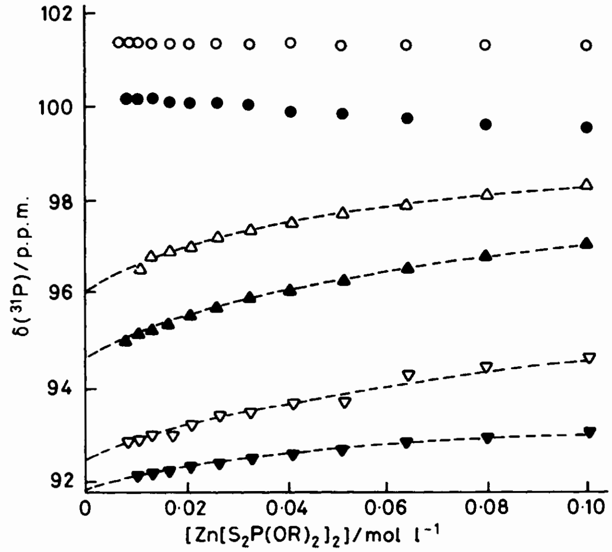
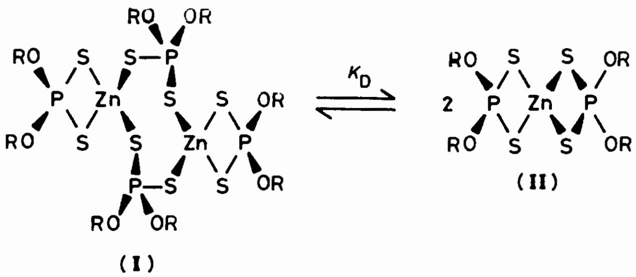


Figure 2. Plots of $\delta(^{31}P)$ against concentration for solutions of $Zn[S_2P(OEt)_2]_2$ in ethanol (○), thf (●), $CDCl_3$ (△), and toluene (▲), and $Zn[S_2P(OPr^i)_2]_2$ in $CHCl_3$ (▼) and toluene (▽). Dashed lines represent calculated $\delta(^{31}P)$ values in terms of monomer–dimer equilibria (see text)

bridging $S_2P(OR)_2$ ligands.[17] Values for the dissociation constants fall in the range 0.018—0.072 mol l^{-1}, indicating that the dimeric species predominate under these conditions, but are larger in toluene than in chloroform. The greater magnitude of



the dissociation constants for the Pr^i derivative over those of the Et are consistent with the increased steric requirements of this group. The value of K_D for the Pr^i derivative in toluene (7.17×10^{-2} mol l^{-1}) compares favourably with that (9×10^{-2} mol l^{-1}) determined by Dakternieks and Graddon[18] in benzene solution from molecular weight data.

The chemical shifts of the Et derivative in the donating solvents ethanol and tetrahydrofuran (thf) are significantly higher than those observed in toluene and chloroform, but are lower than values (> 107 p.p.m.) proposed by Glidewell[17] for ionic *O,O'*-dialkyl dithiophosphato species. That in ethanol is essentially constant at *ca.* 101.3 p.p.m. over the whole of the concentration range studied, whereas in thf the shift increases somewhat from 99.5 to 100.2 p.p.m. These values are similar to those observed for the pyridine complex, $Zn[S_2P(OEt)_2]_2 \cdot py$ (see later), and suggest that donor–acceptor complex formation is occurring in these solvents. However, conductance measurements show that the conductance increases greatly in the order toluene [$\log_{10}$ (molar conductance, Λ_M)] toluene

Table 3. Calculated values of chelating (δ_c) and bridging (δ_b) ^{31}P chemical shifts and dissociation constants (K_D)

Compound	Solvent	δ_c/ p.p.m.	δ_b/ p.p.m.	10^2K_D/ mol l^{-1}	χ^2*
$Zn[S_2P(OEt)_2]_2$	$CDCl_3$	96.0	106.3	1.81	6.1
$Zn[S_2P(OEt)_2]_2$	$C_6H_5CH_3$	94.6	108.7	3.08	2.9
$Zn[S_2P(OPr^i)_2]_2$	$CHCl_3$	91.9	100.0	4.45	0.3
$Zn[S_2P(OPr^i)_2]_2$	$C_6H_5CH_3$	92.5	112.4	7.17	59.2

* Final sum of squares ($\times 10^3$).

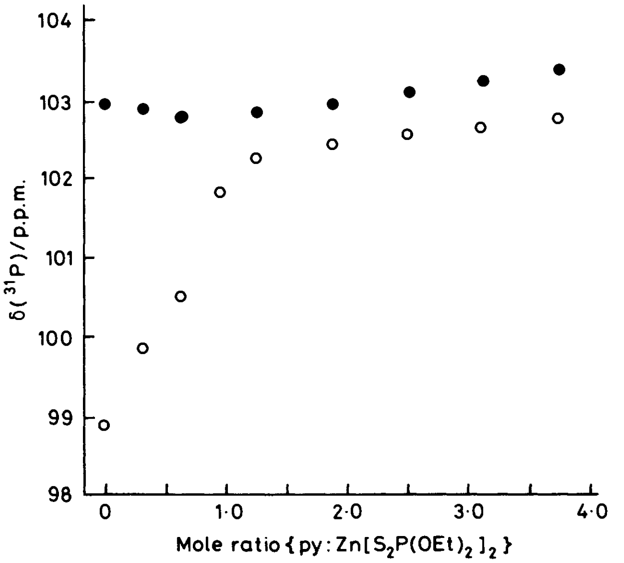


Figure 3. Plots of $\delta(^{31}P)$ against py:$Zn[S_2P(OEt)_2]_2$ mol ratio in ethanol (●) and toluene (○) solution (0.1 mol dm^{-3})

(−8.1) < thf (−6.0) < EtOH (−4.2), indicating that some ionization of the dithiophosphato ligands is occurring, which would, if in rapid dynamic equilibrium with the covalently-bound ligands, also give rise to an increased chemical shift.

Complexation of Zinc(II) Bis(O,O′-*dialkyl dithiophosphates*) *by Nitrogen-donor Molecules*.—Titration of pyridine into a toluene solution of $Zn[S_2P(OEt)_2]_2$ (0.1 mol dm^{-3}) results in an initial sharp movement to higher frequency of the ^{31}P resonance until a pyridine–zinc ratio of 1:1 is reached. At this point a sharp discontinuity occurs, after which the addition of further pyridine causes only relatively minor change. When the same titration is carried out in ethanol solution, a shallow but distinct minimum in the ^{31}P chemical shift is observed for both the Et and Pr^i derivatives at the same mol ratio of reactants (Figure 3). These data show that the 1:1 complex $Zn[S_2P(OR)_2]_2\cdot py$ (R = Et or Pr^i) is formed in solution, and, since only one ^{31}P resonance is observed, that rapid intermolecular ligand exchange involving both the parent complex $Zn[S_2P(OR)_2]_2$ (both monomer and dimer) and the pyridine complex occurs. We have previously[12] isolated the pyridine and several other 1:1 complexes of zinc bis(*O,O*′-dialkyl dithiophosphates) with nitrogen donors, and ^{31}P chemical shift data for these as 0.05 mol dm^{-3} solutions in $CDCl_3$ and toluene are collected in Table 4. The additional inductive effect of the Pr^i group produces a 3—4 p.p.m. shift to lower frequency of the ^{31}P resonance in all the complexes. A solvent effect of 1.5—2 p.p.m. between the two solvents is also observed. However, for both series of complexes, a general monotonic shift of the resonance to a higher frequency occurs as the number of nitrogen-donor atoms in the ligand increases.

Table 4. ^{31}P Chemical shift data for zinc(II) *O,O*′-dialkyl dithiophosphates and complexes

	$\delta(^{31}P)$/p.p.m.	
Compound[a,b]	$CDCl_3$ Solution[c]	$C_6H_5CH_3$ Solution[d]
$Zn[S_2P(OEt)_2]_2$	96.9	97.87
$Zn[S_2P(OEt)_2]_2\cdot py$	100.2	101.80
$Zn[S_2P(OEt)_2]_2\cdot bipy$	102.7	104.20
$Zn[S_2P(OEt)_2]_2\cdot deen$	103.6	104.94
$Zn[S_2P(OEt)_2]_2\cdot phen$	102.8	104.4[e]
$Zn[S_2P(OEt)_2]_2\cdot terpy$	105.5	[f]
$[Zn(datau)][S_2P(OEt)_2]_2$	110.9[d]	
$Zn[S_2P(OPr^i)_2]_2$	92.4	93.71
$Zn[S_2P(OPr^i)_2]_2\cdot py$	96.7	98.49
$Zn[S_2P(OPr^i)_2]_2\cdot bipy$	99.7	101.43
$Zn[S_2P(OPr^i)_2]_2\cdot deen$	100.6	102.4
$Zn[S_2P(OPr^i)_2]_2\cdot phen$	99.9	101.80[e]
$Zn[S_2P(OPr^i)_2]_2\cdot terpy$	102.8	[f]

[a] Recorded as 0.05 mol l^{-1} monomer solutions. [b] py = Pyridine, bipy = 2,2′-bipyridine, deen = *N,N*′-diethylethylenediamine, phen = 1,10-phenanthroline, terpy = 2,2′:6′,2″-terpyridine, datau = 1,11-diamino-3,6,9-triazaundecane. [c] JEOL FX90Q instrument. [d] Bruker WM250 instrument. [e] Saturated solutions. [f] Insoluble.

It appears from the literature that the factors contributing to the ^{31}P chemical shifts in four-co-ordinate phosphorus compounds are by no means simple or free from controversy. *A priori*, electronic effects such as ligand electronegativity and *d*-orbital occupancy, as well as interrelated structural parameters such as P–X (X = electronegative atom) bond distances and XPX bond angles might, amongst other things, be expected to exert an influence on the magnitude of the ^{31}P chemical shift. Of these, the major contributing factor appears to be the XPX bond angle, variation of which would be expected strongly to affect *d*-orbital occupation and thereby the ^{31}P chemical shift. Indeed, ^{31}P chemical shift data have been observed to correlate with changes in the OPO bond angle in both phosphorus oxyacids[19] and phosphate esters,[20] and the SPS bond angle in 2-t-butyl-2-thioxo-1,3,2-dithiaphosphocane compounds,[21] whilst both Van Wazer and co-workers[22] and Purdela[23] have provided some theoretical justification for these observations.

In the present case, the trend in ^{31}P chemical shift of the complexes is in the opposite sense to that expected on the grounds of increased shielding at phosphorus due to the transmission of electron density through the σ framework from the increasing number of nitrogen-donor ligands. However, an examination of the structural data for the py, 2,2′-bipyridine (bipy), and 2,2′:6′,2″-terpyridine (terpy) complexes of $Zn[S_2P(OPr^i)_2]_2$[12] shows that an increase in the number of nitrogen-donor atoms is accompanied by a change in the mode of attachment of the two dithiophosphato groups to zinc. In the py complex, one dithiophosphate group chelates symmetrically, whereas the other is unidentate, whilst in the terpy complex both are unidentate. In the bipy complex, one is unidentate, but the second chelates in an intermediate, highly anisobidentate, fashion. That only a single ^{31}P resonance is observed for both the py and bipy complexes indicates that both these molecules are fluxional at room temperature. Plots of the ^{31}P chemical shift *versus* the mean SPS bond angles for $Zn[S_2P(OPr^i)_2]_2$ and its complexes are shown in Figure 4, which demonstrates a nearly linear relationship between these two quantities for this series of compounds. Other structural parameters, including the mean OPO bond angle, vary to a much lower extent and in a less systematic manner. We therefore conclude that in these and related complexes the variation in the ^{31}P chemical shift is controlled largely by the change in the SPS bond angle.

The ^{31}P chemical shift for the complex $[Zn(datau)][S_2P(OEt)_2]_2$ (datau = 1,11-diamino-3,6,9-triazaundecane) is exceptionally high at 110.9 p.p.m. We have previously shown that this material exists as discrete cations and anions in the crystal,[12] and would expect a similar constitution in chloroform solution, consistent with the range of chemical shifts (107.0—113.2 p.p.m.) reported for $M[S_2P(OPr^i)_2]$ {M = K^+, $[NH_4]^+$, $[NMe_4]^+$, $[NH_3(C_6H_{11})]^+$, or $[NH_2(C_6H_{11})_2]^+$} in a variety of solvents.[17,24]

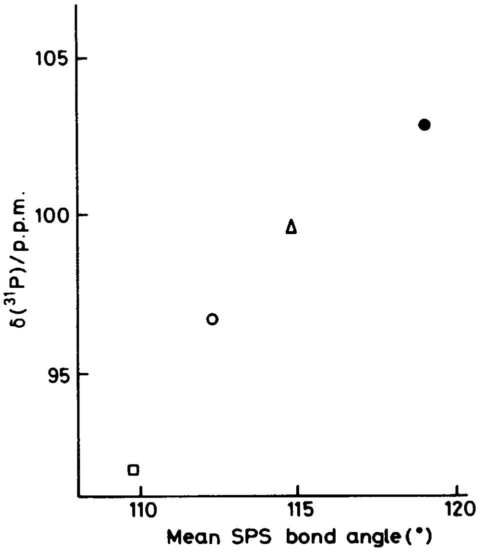


Figure 4. Plot of $\delta(^{31}P)$ against mean SPS bond angle for $Zn[S_2P(OPr^i)_2]_2$ (□) and its 1:1 complexes with py (○), bipy (△), and terpy (●) (0.05 mol dm^{-3} solutions in $CDCl_3$)

The Interconversion of 'Normal' and 'Basic' Zinc(II) *O,O'-Dialkyl Dithiophosphates.*—The dissolution of the analytically-pure 'basic' *O,O'*-dialkyl dithiophosphato zinc(II) derivatives, $Zn_4[S_2P(OR)_2]_6O$ (R = Et or Pr^i), in $CDCl_3$ results in solutions which exhibit ^1H n.m.r. spectra of both the 'basic' and 'normal' compounds [Figure 1(*a*) and (*b*)], due to the facile equilibrium (1).

$$Zn_4[S_2P(OR)_2]_6O \rightleftharpoons 3\,Zn[S_2P(OR)_2]_2 + ZnO \quad (1)$$

In this solvent, significant quantities of the 'normal' compound are present at room temperature immediately upon dissolution, with the amount steadily increasing over a period of 8 h to *ca.* 40% conversion. In toluene as solvent, however, dissociation occurs to a much lower extent. Figure 5 illustrates the effect of increasing temperature upon a solution of $Zn_4[S_2P(OPr^i)_2]_6O$ in toluene. At 293 K only a very weak broad resonance of the 'normal' compound at 94.9 p.p.m. is discernible in addition to the triplet at 100.8 p.p.m. due to the 'basic' compound, but as the temperature is increased, the intensity of the resonance due to the 'normal' compound increases significantly. After 4 h at 353 K, both resonances have approximately the same intensity and zinc oxide is also observed to precipitate from solution. On standing at room temperature the dissociation is reversed, and only a small amount of the 'normal' compound is present after 21 d. At temperatures of > 343 K the spectra also contain an additional though much weaker third resonance at 102.8 p.p.m. The magnitude of this chemical shift and that for the 'basic' zinc(II) *O,O'*-dialkyl dithiophosphate indicate ligand SPS bond angles of > 115°, consistent with a bridging bonding mode similar to that observed in the structure of $Zn_4[S_2P(OEt)_2]_6S$.[11] The third resonance at 102.8 p.p.m. we attribute to an intermediate formed in the rupture of the $Zn_4[S_2P(OPr^i)_2]_6O$ cage to afford 'normal' $Zn[S_2P(OPr^i)_2]_2$ and zinc(II) oxide. We would expect the conversion of 'basic' to 'normal' to proceed in a stepwise manner involving the successive elimination of

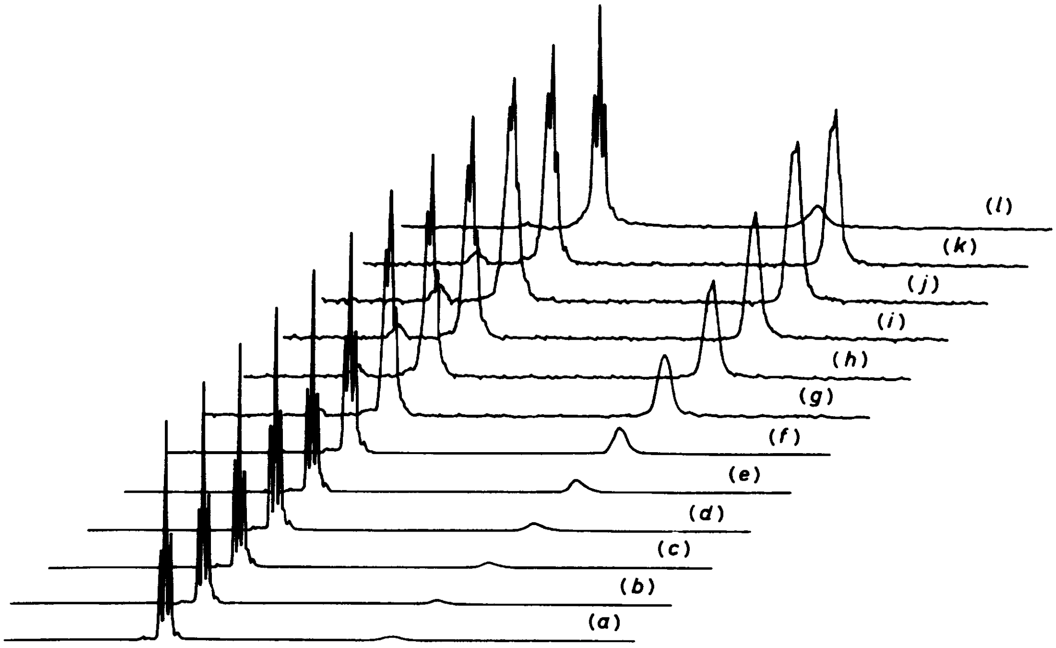


Figure 5. The effect of temperature on the ^{31}P n.m.r. spectrum of a solution of $Zn_4[S_2P(OPr^i)_2]_6O$ (0.05 mol dm^{-3}) in toluene: (*a*) 293, (*b*) 303, (*c*) 313, (*d*) 323, (*e*) 333, (*f*) 343, (*g*) 353, (*h*) 353 K after 1 h, (*i*) 353 K after 2 h, (*j*) 353 K after 3 h, (*k*) 353 K after 4 h, (*l*) room temperature after 21 d

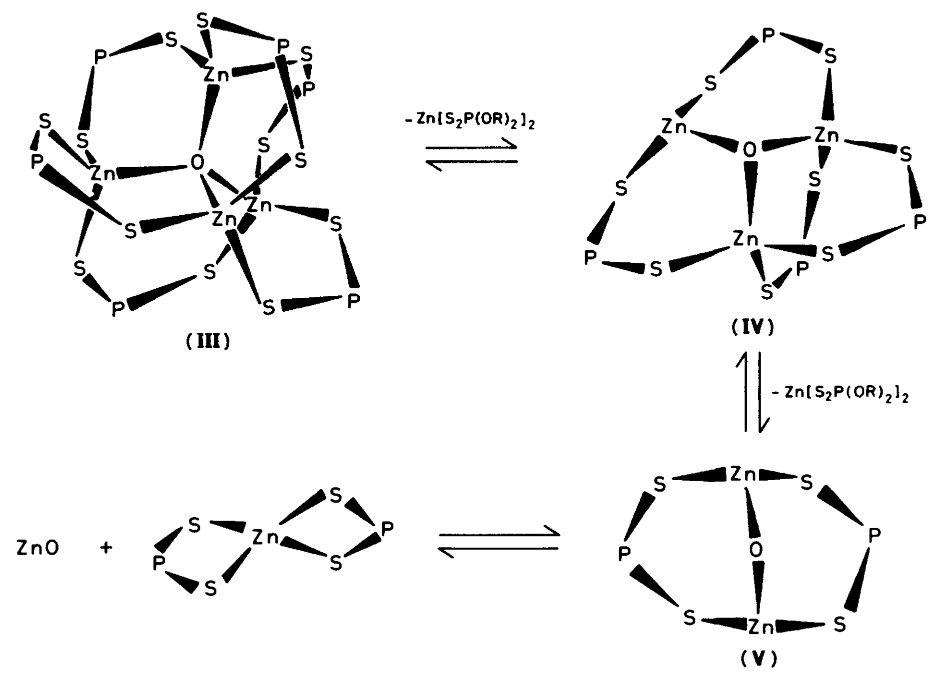


Figure 6. Schematic representation of the breakdown of the 'basic' $Zn_4[S_2P(OR)_2]_6O$ cage. The alkoxy groups attached to phosphorus have been omitted for clarity

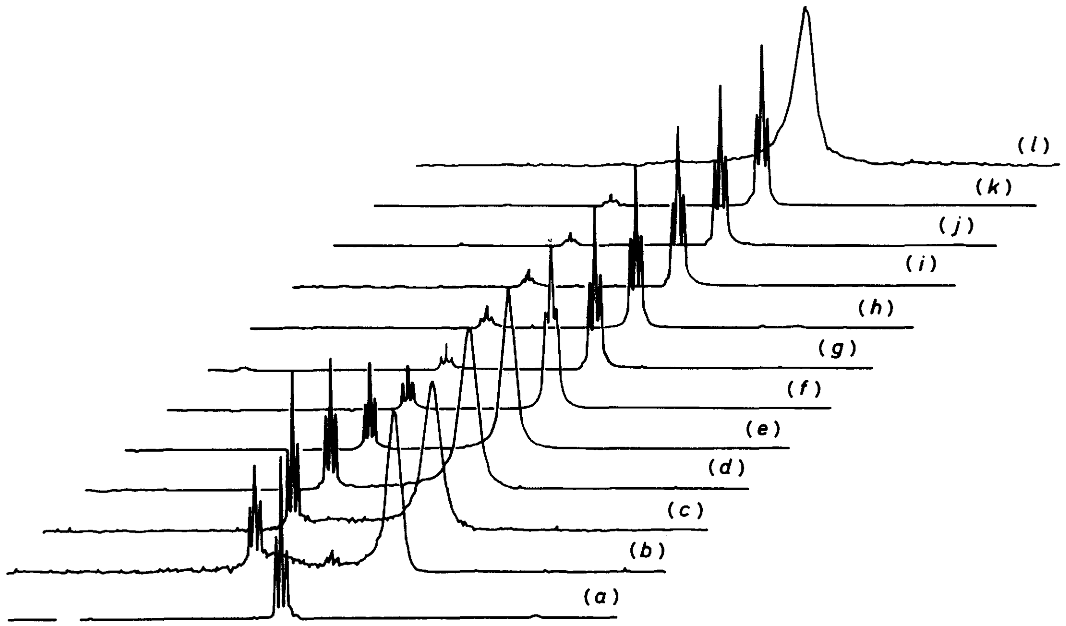


Figure 7. The effect of added pyridine on the ^{31}P n.m.r. spectrum of $Zn_4[S_2P(OPr^i)_2]_6O$ (0.05 mol dm^{-3}) in toluene: (*a*) neat compound at 303 K, (*b*) 303 K, py (3 mol) added; subsequent spectra taken at (*c*) 313 K, (*d*) 323 K, (*e*) 333 K, (*f*) 343 K, (*g*) 353 K, (*h*) 353 K after 1 h, (*i*) 353 K after 2 h, (*j*) 353 K after 3 h, (*k*) 353 K after 4 h, (*l*) room temperature after 28 d

$Zn[S_2P(OR)_2]_2$ molecules from the $Zn_4[S_2P(OR)_2]_6O$ cage (III) as illustrated in Figure 6. In this figure, two intermediates, (IV) and (V), are proposed. Whilst the latter would be expected spontaneously to eliminate ZnO, models of the former show it to be without significant strain, and it is to this species that we ascribe the resonance observed at 102.8 p.p.m.

The cleavage of the $Zn_4[S_2P(OR)_2]_6O$ cage is greatly accelerated by the presence of nitrogen donors. Figure 7 shows the effect of added pyridine on the ^{31}P n.m.r. spectrum of a solution of 'basic' $Zn_4[S_2P(OPr^i)_2]_6O$ in toluene. Upon addition of pyridine, the spectrum [Figure 7(*a*)] of the 'basic' compound containing a small equilibrium amount of the 'normal' compound virtually completely disappears, with new resonances appearing at 99.3 p.p.m. (broad and unresolved) due to $Zn[S_2P(OPr^i)_2]_2{\cdot}py$ and at 102.6 p.p.m. (sharply resolved triplet) due to intermediate (IV). Subsequent heating of the sample decreases the amount of intermediate present in solution to a very small amount at 353 K, when the resonance due to the

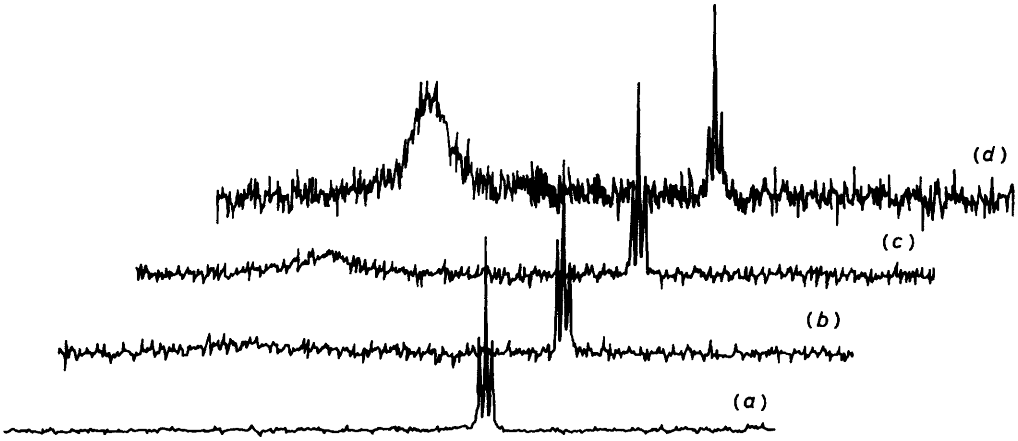
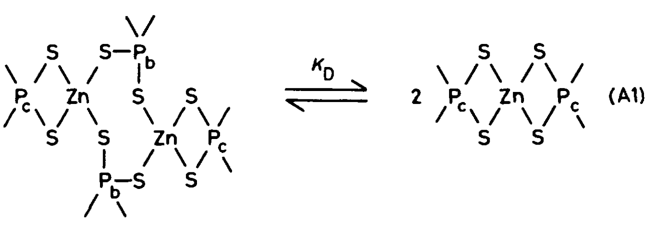


Figure 8. The effect of added 2,2′:6′,2″-terpyridine on the ^{31}P n.m.r. spectrum of $Zn[S_2P(OPr^i)_2]_6O$ (0.05 mol dm^{-3}) in toluene: (*a*) neat compound at 303 K, (*b*) 303 K, 2,2′:6′,2″-terpyridine (3 mol) added; subsequent spectra taken at (*c*) 313 K and (*d*) 323 K

pyridine complex has resolved also into a well defined triplet. No reconversion to the 'basic' compound is observed under these conditions, even after allowing the sample to stand at room temperature for 28 d. A similar, though less marked, decomposition is observed upon the addition of terpy to a similar toluene solution of 'basic' $Zn_4[S_2P(OPr^i)_2]_6O$ (Figure 8). In this case decomposition is much slower, and the product, $Zn[S_2P(OPr^i)_2]_2\cdot$terpy begins to precipitate out of solution at an early stage which accounts for the rather lower spectral quality.

Appendix

Interpretation of the concentration-dependent ^{31}P n.m.r. chemical shift data for zinc(II) bis(*O,O′*-dialkyl dithiophosphates) in terms of a monomer–dimer equilibrium is given here.


(A1)

The monomer–dimer equlibrium may be represented by equation (A1), where P_b and P_c represent phosphorus atoms in bridging and chelating $S_2P(OR)_2$ ligands, respectively. Assuming negligible change in the geometry and ^{31}P chemical shift of the chelating $S_2P(OR)_2$ ligands in both dimer and monomer molecules, the observed change in ^{31}P chemical shift on change in concentration can be attributed to the conversion of the two bridging $S_2P(OR)_2$ ligands of the dimer to two chelating $S_2P(OR)_2$ ligands in the monomers.

For a solution of overall concentration m (in terms of dimer molecules), at equilibrium with a degree of dissociation, α, the concentration of monomer molecules present = $2m\alpha$. The concentration of bridging $S_2P(OR)_2$ ligands (P_b sites) at equilibrium = $2m(1 - \alpha)$, and the concentration of chelating (P_c) sites in monomer molecules formed by conversion from bridging $S_2P(OR)_2$ ligands in dimer molecules = $2m\alpha$. Therefore the total concentration of chelating sites = $2m + 2m\alpha = 2m(1 + \alpha)$. Total number of sites = $4m$. Hence, the dissociation constant, K_D, derived by observation of the ^{31}P chemical shift, is given by equation (A2).

$$K_D = \frac{(\text{Concn. of converted } P_c \text{ sites in monomer molecules})^2}{(\text{Concn. of bridging } P_b \text{ sites in dimer molecules})} = \frac{(m\alpha)^2}{2m(1-\alpha)} = \frac{m\alpha^2}{2(1-\alpha)} \tag{A2}$$

Since only a single ^{31}P resonance is observed, exchange of $S_2P(OR)_2$ ligands between dimer and monomer molecules is rapid on the n.m.r. time-scale, and the chemical shift ($\delta_{calc.}$) will be given by the expression (A3), where δ_b and δ_c are the chemical

$$\delta_{calc.} = f(^{31}P_b)\cdot\delta_b + f(^{31}P_c)\cdot\delta_c \tag{A3}$$

shifts of ^{31}P nuclei in bridging and chelating $S_2P(OR)_2$ ligands, respectively, and where $f(^{31}P_b)$ and $f(^{31}P_c)$ are given by (A4) and (A5). Therefore, $\delta_{calc.}$ is given by (A6).

$$f(^{31}P_b) = \frac{\text{Number of bridging sites}}{\text{Total number of sites}} = \frac{2m(1-\alpha)}{4m} = \frac{1-\alpha}{2} \tag{A4}$$

$$f(^{31}P_b) = \frac{\text{Number of chelating sites}}{\text{Total number of sites}} = \frac{2m(1+\alpha)}{4m} = \frac{1+\alpha}{2} \tag{A5}$$

$$\delta_{calc.} = \frac{(1-\alpha)\delta_b}{2} + \frac{(1+\alpha)\delta_c}{2} \tag{A6}$$

Substitution of α from equation (A2) in equation (A6) yields an expression for δ_{calc} in terms of m, K_D, δ_b, and δ_c. Computed values of K_D, δ_b, and δ_c are obtained by minimising the error-square sum $\Sigma(\delta_{calc.} - \delta_{expt.})^2$ for various values of m and $\delta_{expt.}$, the experimentally observed chemical shift.

Acknowledgements

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