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The nature of zinc(II) bis(*O,O'*-dialkyl dithiophosphates) in ethanol: complexation or ionisation?

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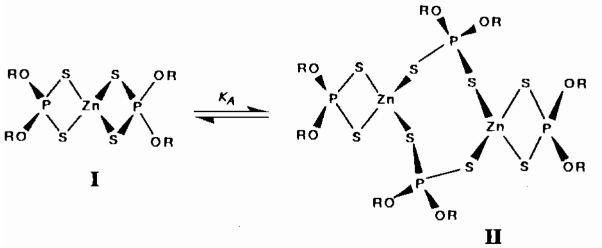
Abstract

^{31}P NMR chemical shift data have been recorded for eight zinc(II) bis(*O,O'*-dialkyl dithiophosphates) ($Zn(S_2P(OR)_2)_2$) (R = n-Bu, iso-Bu, sec-Bu, n-Pent, n-Hex, n-Oct, n-Non and n-Dec) in ethanol. Apart from sec-BuZnDDP which exhibits a chemical shift of *c.* 100.1 ppm, the chemical shifts in ethanol solution are essentially independent of the alkyl group and fall in the narrow range 103.3–104.0 ppm in the concentration range 0–0.1 M. The conductance of both n-BuZnDDP and n-HexZnDDP in ethanol increases smoothly and steadily with increasing concentration. In toluene, however, the conductance of both is three or four orders of magnitude lower than in ethanol and very similar to that of neat toluene, indicating that in ethanol some ionisation of the DDP ligands occurs, whereas toluene solutions are non-conducting. Ethanol solutions of ZnDDPs comprise principally adducts of the type $Zn(S_2P(OR)_2)_2 \cdot 2EtOH$, superimposed on which is a small extent of ionisation.

Introduction

Our previous studies have shown that the range of ^{31}P NMR chemical shifts observed for solutions of zinc(II) bis(*O,O'*-dialkyl dithiophosphates) (ZnDDPs) in non-donating solvents such as toluene, chloroform and poly(alphaolefin) (a low viscosity, high molecular weight hydrocarbon solvent) is readily interpreted in terms of the monomer ⇌ dimer equilibrium.



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II

(1)

The position of the equilibrium as shown by the value of the association constant, k_A, is dependent upon the nature of the alkyl group R on the DDP ligand and the nature of the solvent [1]. Values of k_A are significantly higher in poly(alphaolefin) solution than in chloroform or toluene, but show that in all three solvents the dimer predominates. In more polar donor solvents such as ethanol it is obvious that such a relatively simple situation does not exist, and in this paper we discuss the constitution of ZnDDPs in ethanol.

Experimental

The synthesis of the zinc(II) bis(*O,O'*-dialkyl dithiophosphates) and the general procedures have been reported elsewhere [1]. For each of the ZnDDP–solvent systems studied, a series of solutions was made up using volumetric glassware. The composite-pulse proton-decoupled ^{31}P NMR spectrum of each solution was recorded at ambient temperature using a Bruker WM250 Fourier transform NMR spectrometer. All chemical shifts are quoted with respect to 85% phosphoric acid solution at 297 K using an internal D_2O lock.

Solution of the appropriate ZnDDP (*c.* 0.1 mol l^{-1}) were made up accurately in either ethanol or toluene as required and diluted repetitively to produce the desired range of concentrations. The relative conductance of each solution was measured using a Wayne Kerr bridge at ambient temperature.

Results and discussion

Only a single ^{31}P resonance is observed for solutions of all the ZnDDPs, ($Zn(S_2P(OR)_2)_2$ (R = n-Bu, iso-Bu, sec-Bu, n-Pent, n-Hex, n-Oct, n-Non and n-Dec), in ethanol indicative of either the presence of equivalent DDP groups or a rapid dynamic exchange of inequivalent DDP groups. The magnitudes of the chemical shifts of these resonances are somewhat higher than the

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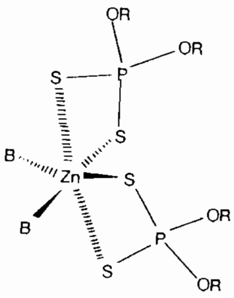
TABLE 1. ^{31}P chemical shift data for zinc(II) bis(*O,O'*-dialkyl dithiophosphates) $(Zn(S_2P(OR)_2)_2)$ (R = n-Bu, iso-Bu, sec-Bu, n-Pent, n-Hex, n-Oct, n-Non and n-Dec[a]) in various solvents

R	n-Bu	iso-Bu	sec-Bu	n-Pent	n-Hex	n-Oct	n-Non	n-Dec
Ethanol								
Conc. range[b]	0.0083–0.0998	0.0084–0.1009	0.0083–0.1004	0.0088–0.1060	0.0077–0.0924	0.0083–0.0984	0.0077–0.0900	0.0084–0.1009
$\delta(^{31}P)$ range	103.64–103.51	103.70–103.55	100.15–100.01	103.60–103.50	104.00–103.68	103.92–103.48	103.62–103.42	103.64–103.28
Toluene[c]								
Conc. Range[b]	0.0074–0.0898	0.0100–0.0806	0.0062–0.0762	0.0063–0.0759	0.0072–0.0806	0.0078–0.0889	0.0078–0.0940	0.0077–0.0928
$\delta(^{31}P)$ range	97.51–99.28	98.35–99.81	93.46–94.56	97.36–99.11	97.45–99.27	97.43–99.23	97.43–99.13	97.30–99.13
Chloroform[c]								
Conc range[b]	0.0078–0.0938	0.0100–0.0806	0.0072–0.0864	0.0066–0.0806	0.0072–0.0868	0.0098–0.0914	0.0078–0.0940	0.0112–0.0926
$\delta(^{31}P)$ range	97.01–98.50	97.77–98.93	93.03–93.93	96.98–98.55	97.29–98.70	97.52–98.67	97.48–98.69	97.55–98.69
Poly(alphaolefin)[c]								
Conc. range[b]	0.0078–0.0942	0.0086–0.1031	0.0664–0.686	0.0063–0.0768	0.0043–0.0433	0.0076–0.0868	0.0081–0.0979	0.0069–0.0862
$\delta(^{31}P)$ range	99.21–100.90	99.45–101.08	92.78–94.33	98.86–100.69	98.69–100.39	96.69–98.41	98.91–100.49	99.02–100.49

[a] n-Bu = n-Butyl, iso-Bu = iso-Butyl, sec-Bu = sec-Butyl, n-Pent = n-Pentyl, n-Hex = n-Hexyl, n-Oct = n-Octyl, n-Non = n-Nonyl and n-Dec = n-Decyl. [b] Mol l^{-1}. [c] Data from ref. 1.

corresponding shifts in solvents of lower polarity, and are remarkably invariant with concentration (cf. the behaviour in toluene, chloroform and poly(alphaolefin) [1] (Table 1). Apart from sec-BuZnDDP which exhibits a chemical shift of *c.* 100.1 ppm, the chemical shifts in ethanol solution are essentially independent of the alkyl group and fall in the narrow range 103.3–104.0 ppm in the concentration range 0–0.1 M. Values in this range are, however, not consistent with those expected for such a monomer ⇌ dimer equilibrium, but instead indicate complex formation involving coordination at the zinc atom.

Our earlier ^{31}P MAS-NMR studies [2] of a wide range of zinc(II) *O,O'*-dialkyl dithiophosphate complexes with amine donor molecules many of known structure have shown that the $\delta(^{31}P)$ chemical shift of the *O,O'*-dialkyl dithiophosphate group can be used as an indication of its bonding mode to the zinc atom. Thus, values of $\delta(^{31}P) < c.$ 100 ppm are indicative of symmetrically bridging or chelating groups, values between *c.* 100 and *c.* 105 ppm anisobidentate chelating, values *c.* 106 ppm unidentate, and values $> c.$ 110 ppm corresponding to ionic *O,O'*-dialkyl dithiophosphate. In the present case, therefore, the ^{31}P chemical shift values observed in ethanol correspond to an anisobidentate chelating mode of bonding of the DDP ligands to the zinc resulting from coordination of two donor atoms to the metal centre as in **III** similar to the geometry adopted in the complex $Zn[S_2P(O^iPr)_2]_2 \cdot bipy$ [3].



III (B = EtOH)

An alternative rationalisation of the high chemical shifts observed in ethanol is that ionisation of the DDP ligands from zinc occurs.

$$Zn[S_2P(OR)_2]_2 + n\text{EtOH} \longrightarrow [Zn(EtOH)_n]^{2+}[S_2P(OR)_2]_2^- \quad (2)$$

Ionisation of DDP from zinc in this fashion is known to occur with multidentate amines, and chemical shift values for ionic DDP species occur at *c.* 110 ppm [3, 4]. The low chemical shift values observed would therefore necessarily have to be ascribed to rapid dynamic equilibration between ionic and covalently bound DDP. If this process were to be the case in ethanol solution because of the high abundance of donors, then an

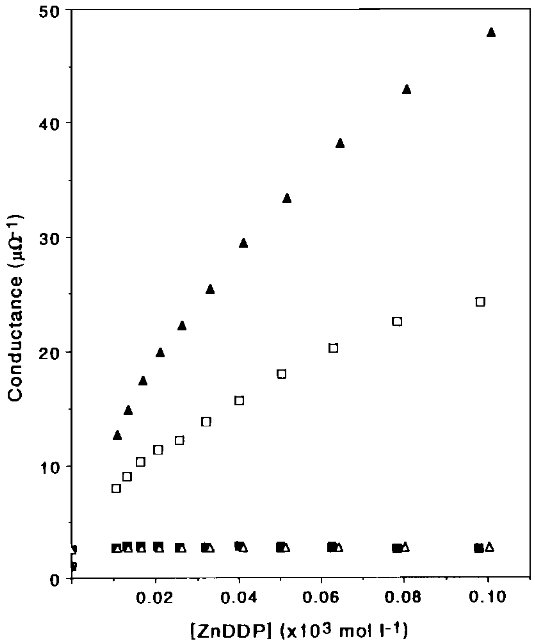


Fig. 1. Plots of conductance vs. concentration for n-BuZnDDP in ethanol (□), n-BuZnDDP in toluene ($\times 10^3$) (■), n-HexZnDDP in ethanol (▲), and n-HexZnDDP in toluene ($\times 10^3$) (△).

increase in molar conductance values of the solutions should be readily apparent.

Plots of conductance versus concentration for the four systems n-BuZnDDP in ethanol, n-BuZnDDP in toluene, n-HexZnDDP in ethanol, and n-HexZnDDP in toluene are shown in Fig. 1. In ethanol, the conductance of both n-BuZnDDP and n-HexZnDDP increases smoothly and steadily with increasing concentration. Even at the lowest concentrations measured (*c*. 0.01 mol l^{-1}) there was an approximately eightfold increase in conductance for n-BuZnDDP compared to that of neat ethanol and an approximately twelvefold increase for n-HexZnDDP. In toluene, however, the conductance of both the ZnDDPs is three or four orders of magnitude lower than in ethanol and very similar to that of neat toluene, and remains essentially constant over the concentration range studied. These observations indicate that in ethanol some ionisation of the DDP ligands occurs, whereas toluene solutions are non-conducting.

What then is the constitution of ethanol solutions of ZnDDPs? The ^{31}P chemical shift values in ethanol are consistent with simple adduct formation rather than ionisation. However, conductance measurements in ethanol and toluene indicate the formation of ionic species in the former solvent and hence the occurrence of ionisation to some extent. In contrast to the situation with multidentate amines where total ionisation of DDP ligands occurs [4], the chemical shift values show that in ethanol it is obvious that ionisation can only occur to a relatively small extent. Although essentially invariant with concentration, all the ZnDDP solutions in ethanol do show a small *decrease* in the ^{31}P chemical shift with increasing ZnDDP concentration, an anomalous observation considering that the conductance *increases* with increasing concentration. Our conclusion, therefore, is that ethanol solutions of ZnDDPs comprise principally adducts of the type **III**, superimposed on which is a small extent of ionisation according to eqn. (2).

Acknowledgements

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