Lead-207 Chemical Shift Data for Bivalent Lead Compounds: Thermodynamics of the Equilibrium $Pb(O_2CCH_3)_2 \rightleftharpoons [Pb(O_2CCH_3)]^+ + O_2CCH_3^-$ in Aqueous Solution in the Temperature Range 303—323 K

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Lead-207 n.m.r. chemical shift data have been recorded for the following bivalent lead compounds (solvent in parentheses): $Pb(NO_3)_2$ (water), $Pb(ClO_4)_2{\cdot}3H_2O$ (water), $Pb(O_2CCH_3)_2{\cdot}3H_2O$ (water), $Pb(O_2CC_6F_5)_2$ (tetrahydrofuran, thf), $Pb[S_2P(OR)_2]_2$ (R = C_2H_5 or i-C_4H_9) (thf and dichloromethane). The nature of the solution species is discussed. The very high-field chemical shifts exhibited by the hydrated lead(II) dication and the monoacetato- and mononitrato-lead(II) monocations are ascribed to efficient nuclear shielding resulting from the confinement of the lead(II) lone pair to the metal 6*s* orbital. Chemical shifts of the other species occur at much lower field, and structures in which the lone pair is stereochemically active and occupying a hybrid sp^3d^n orbital are proposed. Analysis of the concentration-dependence data has been employed to evaluate the association constant at 298 K, $K_{assoc.}$, of $[Pb(NO_3)]^+$ (1.233 $dm^3\ mol^{-1}$), and the dissociation constant at 298 K, $K_{dissoc.}$, of $Pb(O_2CCH_3)_2$ (0.0139 mol dm^{-3}), for the aqueous lead(II) nitrate and acetate systems, respectively. Data for the systems $Pb(O_2CC_6F_5)_2$(tetrahydrofuran) and $Pb[S_2P(OEt)_2]_2$(dichloromethane) have been interpreted in terms of a dimer $\rightleftharpoons$ monomer equilibrium, with dissociation constants at 298 K of the dimer, $K_{dissoc.}$, of 0.143 and 0.268 mol dm^{-3}, respectively. The concentration-independent chemical shift of the lead(II) dithiophosphoridates in tetrahydrofuran is ascribed to the formation of a stable thf solvate in solution. Thermodynamic data for the equilibrium $Pb(O_2CCH_3)_2 \rightleftharpoons [Pb(O_2CCH_3)]^+ + O_2CCH_3^-$ in aqueous solution at 298 K have been evaluated as $\Delta H_{298} = -14.2$ kJ mol^{-1}, $\Delta G_{298} = 10.5$ kJ mol^{-1}, and $\Delta S_{298} = -82.95$ J K^{-1} mol^{-1}.

In recent years the direct observation of a magnetically active metal centre has contributed significantly towards the characterisation of the species present.

Observed lead-207 chemical shifts in solution span a very large range of almost 4 000 p.p.m., and are very sensitive to subtle changes in electronic distribution about the metal; even very small structural changes induce relatively large changes in chemical shift. By far the majority of such data reported to date are for organolead(IV) compounds,[1-4] and from an analysis of the available data the following trends may be inferred: increasing ligand electronegativity decreases the shielding at lead, the presence of electropositive or unsaturated ligands such as aryl, alkynyl, or vinyl increases the shielding, whilst increasing the co-ordination number at lead results in greatly increased shielding.

Our interest in the interaction of lead with biologically relevant molecules in solution has prompted us to investigate the usefulness of lead-207 magnetic resonance in such systems, and in this paper we report data concerning the behaviour of some rather simple bivalent lead derivatives.

Experimental

Spectra were obtained at 298 K using a Bruker WM250 Fourier-transform spectrometer with superconducting magnet. An external deuterium lock was employed and samples were contained in tubes 10 mm in diameter. The central frequency for the lead-207 resonance was 52.330 MHz and the resonance of tetramethyllead was taken as 0 p.p.m. for referencing all measurements. [The absolute frequency for ^{207}Pb in $PbMe_4$ for a field strength giving a ^1H resonance at 250 MHz is Ξ = 52.301 492(10) MHz.] By convention, chemical shifts to a high field (low frequency) of the standard are denoted as negative. Solvents were freshly distilled and dried before use and triply distilled deionised water was employed for aqueous manipulations.

Equilibrium constants, *K*, for the systems (1)—(4) were

$$[Pb(NO_3)]^+ \rightleftharpoons Pb^{2+} + NO_3^- \qquad (1)$$

$$Pb(O_2CCH_3)_2 \rightleftharpoons [Pb(O_2CCH_3)]^+ + O_2CCH_3^- \qquad (2)$$

$$[Pb(O_2CC_6F_5)_2]_2 \rightleftharpoons 2Pb(O_2CC_6F_5)_2 \qquad (3)$$

$$\{Pb[S_2P(OEt)_2]_2\}_2 \rightleftharpoons 2Pb[S_2P(OEt)_2]_2 \qquad (4)$$

evaluated by conventional procedures minimising ($\delta_{obs.} - \delta_{calc.}$) using $\delta_{calc.} = \sum_i m_i\delta_i$, where m_i and δ_i are the mole fraction and chemical shift of the *i*th component, and $K_{dissoc.}$ of $Pb(NO_3)^+ = m\alpha(1 + \alpha)/(1 - \alpha)$ and $K_{dissoc.}$ of $Pb(O_2CCH_3)_2 = K_{dissoc.}$ of dimer $= m\alpha^2/(1 - \alpha)$, where α is the degree of dissociation at concentration *m* of the solute. Calculated chemical shift values are shown in parentheses in Table 1.

Results and Discussion

Lead-207 chemical shift data for the following bivalent lead compounds (solvent in parentheses) are collected in Table 1: $Pb(NO_3)_2$ (water), $Pb(ClO_4)_2{\cdot}3H_2O$ (water), $Pb(O_2CCH_3)_2{\cdot}3H_2O$ (water), $Pb(O_2CC_6F_5)_2$ (tetrahydrofuran, thf), $Pb[S_2P(OEt)_2]_2$ (thf), (CH_2Cl_2), and $Pb[S_2P(OBu^i)_2]_2$ (thf), (CH_2Cl_2). Plots of lead-207 chemical shift *versus* concentration for each system are shown in Figure 1. The range of observed shifts is very large, covering almost 3 000 p.p.m. to high field of the arbitrary reference datum, tetramethyllead. All spectra comprised a single resonance indicative of either a single lead species, or more than one in a dynamic equilibrium which is rapid on the n.m.r. time-scale. The data for each system will be discussed individually.

$Pb(ClO_4)_2{\cdot}3H_2O$-*Water*.—Aqueous solutions of lead(II) perchlorate are known to be totally ionised over the whole of

Table 1. Lead-207 chemical shift data *

$\delta(^{207}Pb)$	Concentration (mol dm^{-3})	$\delta(^{207}Pb)$	Concentration (mol dm^{-3})
(*a*) $Pb(NO_3)_2$–water			
−2 854 (−2 857)	0.010	−2 900 (−2 902)	0.183
−2 864 (−2 863)	0.025	−2 903 (−2 905)	0.201
−2 875 (−2 871)	0.050	−2 907 (−2 908)	0.223
−2 887 (−2 886)	0.105	−2 911 (−2 912)	0.251
−2 889 (−2 889)	0.118	−2 917 (−2 917)	0.287
−2 891 (−2 891)	0.125	−2 932 (−2 929)	0.402
−2 892 (−2 892.5)	0.134	−2 941 (−2 938.5)	0.503
−2 895 (−2 897)	0.155	−2 961 (−2 963)	1.000
−2 898 (−2 899)	0.167		
(*b*) $Pb(ClO_4)_2\cdot 3H_2O$–water			
−2 878	0.012	−2 855	0.473
−2 877	0.031	−2.850	0.611
−2 874	0.062	−2 847	0.759
−2 872	0.089	−2 839	1.002
−2 871	0.120	−2 834	1.193
−2 869	0.159	−2 827	1.474
−2 866	0.227	−2 820	1.928
−2 863	0.292	−2 814	2.785
		−2 800	3.580
		−2 794	5.012
(*c*) $Pb(O_2CCH_3)_2\cdot 3H_2O$–water			
−1 956 (−1 941)	0.010	−1 414 (−1 419)	0.285
−1 876 (−1 879)	0.014	−1 404 (−1 409)	0.317
−1 733 (−1 778)	0.024	−1 394 (−1 399)	0.357
−1 681 (−1 648)	0.050	−1 380 (−1 387)	0.408
−1 597 (−1 594)	0.070	−1 364 (−1 375)	0.476
−1 559 (−1 542)	0.100	−1 356 (−1 363)	0.571
−1 429 (−1 428)	0.259	−1 350 (−1 345)	0.714
		−1 337 (−1 324)	1.000
(*d*) $Pb(O_2CC_6F_5)_2$–thf			
−959 (−954)	0.061	−1 075 (−1 080)	0.122
−975 (−972)	0.068	−1 128 (−1 123)	0.153
−994 (−994)	0.076	−1 175 (−1 179)	0.204
−1 017 (−1 016)	0.087	−1 258 (−1 257)	0.306
−1 044 (−1 046)	0.102		
(*e*) $Pb[S_2P(OEt)_2]_2$–thf			
−402	0.031		
−402	0.122		
−410	0.245		
−420	0.490		
(*f*) $Pb[S_2P(OEt)_2]_2$–CH_2Cl_2			
−31 (−34)	0.086	−190 (−186)	0.334
−80 (−72)	0.125	−221 (−226)	0.432
−88 (−87)	0.144	−237 (−234)	0.500
−103 (−103)	0.166	−240 (−246)	0.557
−121 (−122)	0.196	−298 (−296)	0.863
−131 (−125)	0.200	−310 (−311)	1.000
−148 (−146)	0.240	−316 (−312)	1.003
−167 (−176)	0.308		
(*g*) $Pb[S_2P(OBu^i)_2]_2$–thf		(*h*) $Pb[S_2P(OBu^i)_2]_2$–CH_2Cl_2	
−412	0.049	−70	0.258
−415	0.098	−127	0.516
−419	0.195		
−427	0.390		

* Relative to tetramethyllead (0 p.p.m.); calculated values in parentheses (see text).

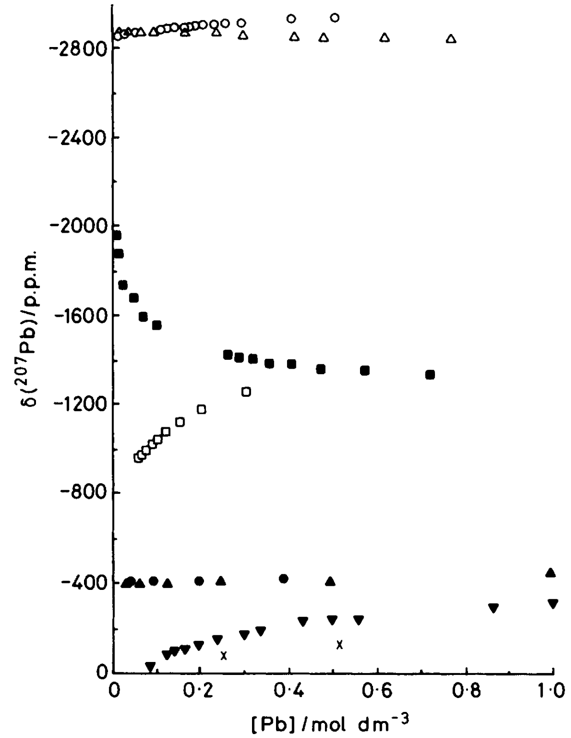

Figure 1. Concentration dependence of the lead-207 chemical shift of (compound–solvent): $Pb(NO_3)_2$–water (○), $Pb(ClO_4)_2\cdot 3H_2O$–water (△), $Pb(O_2CCH_3)_2\cdot 3H_2O$–water (■), $Pb(O_2CC_6F_5)_2$–thf (□), $Pb[S_2P(OEt)_2]_2$–thf (▲), $Pb[S_2P(OEt)_2]_2$–CH_2Cl_2 (▼), $Pb[S_2P(OBu^i)_2]_2$–thf (●), and $Pb[S_2P(OBu^i)_2]_2$–CH_2Cl_2 (×)

the concentration range.[5] Hence, the extreme high-field chemical shift observed (−2 880 p.p.m. at infinite dilution) can be assigned to the hydrated lead(II) cation, $[Pb(H_2O)_n]^{2+}$. The precise value of n, the degree of solvation, is not evaluated. However, our solid-state studies of lead(II) carboxylates and their solvates appear to indicate a preference for eight-co-ordination when oxygen ligands bond to lead(II),[6] although octahedral co-ordination has been characterised in the anti-pyrinelead(II) cation * (gegenion perchlorate).[7] The efficient shielding of the lead nucleus, indicated by the high-field shift, is most probably a result of the localisation of the lead(II) lone pair in the isotropic 6*s* orbital. The slight variation in chemical shift on increase in concentration (−2 880 p.p.m. at infinite dilution, −2 839 p.p.m. at 1 mol dm^{-3} and −2 794 p.p.m. at 5 mol dm^{-3}) may be ascribed to a long-range cation–anion interaction, rather than a water–perchlorate ion ligand exchange with the first co-ordination sphere of the metal, since such a process would result in a shift to higher rather than lower fields (see below).

$Pb(NO_3)_2$–*Water*.—Aqueous solutions of lead(II) nitrate exhibit similar very high-field shifts to those observed for lead(II) perchlorate, but which progress steadily from −2 854 p.p.m. at the lowest concentration studied (0.01 mol dm^{-3}) to −2 961 p.p.m. at 1 mol dm^{-3}. This latter value is in excellent agreement with that (−2 961.2 p.p.m.) measured by Maciel and Dallas.[8] The low-concentration value is close to that shown by solutions of lead(II) perchlorate, and thus is reasonably assigned to the hydrated lead(II) cation. Lead(II) cations and nitrate anions are known to associate even at moderate

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* Antipyrine = 2,3-dimethyl-1-phenyl-3-pyrazolin-5-one.

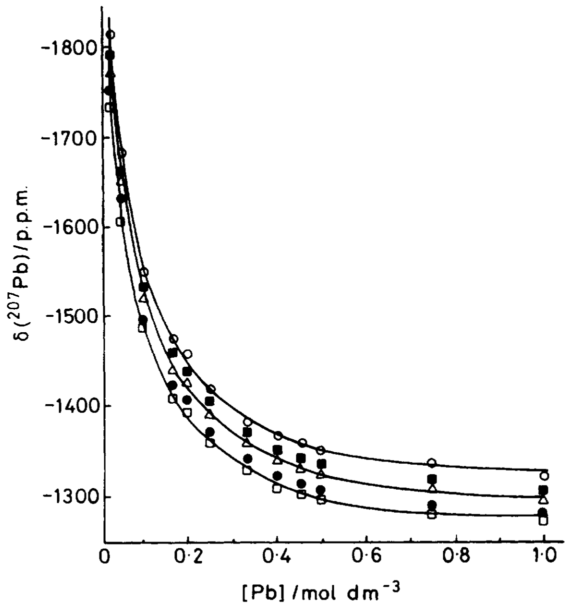

Figure 2. The variation of the lead-207 chemical shift with concentration of aqueous solutions of lead(II) acetate at 303 (○), 309 (■), 313 (△), 319 (●), and 323 K (□). The solid lines represent calculated values; those for 309 and 319 K have been omitted for clarity

concentrations, forming the mononitratolead(II) monocation, with a formation constant of 15.1 at infinite dilution and 2.6 at ionic strength 2.00 mol dm^{-3} at 25 °C.[9,10] The species is again presumably hydrated to achieve co-ordination saturation. In the present case, computer analysis of the data in terms of the equilibrium (5) yields a value of the association constant

$$[Pb(H_2O)_n]^{2+} + NO_3^- \rightleftharpoons [Pb(NO_3)(H_2O)_m]^+ \quad (5)$$

$K_{assoc.} = [Pb(NO_3)(H_2O)_m{}^+]/[Pb(H_2O)_n{}^{2+}][NO_3{}^-]$ of 1.233(1) dm^3 mol^{-1} in the concentration range 0—1 mol dm^{-3} at 25 °C with computed chemical shifts of $-2\,853(2)$ and $-3\,028(2)$ p.p.m. (estimated standard deviations in parantheses) for the two equilibrating species $[Pb(H_2O)_n]^{2+}$ and $[Pb(NO_3)(H_2O)_m]^+$, respectively. The higher field shift calculated for the mononitratolead(II) species is to be expected, since replacement of a water ligand by a more electronegative nitrate group in the first co-ordination sphere of the metal will result in a more polar lead–oxygen (nitrate) bond and a contraction of the lead 6*s* orbital, with a concomitant increase in nuclear shielding.

$Pb(O_2CCH_3)_2{\cdot}3H_2O$–*Water*.—Relatively drastic changes in chemical shift are observed upon dilution of a 1 mol dm^{-3} solution of lead(II) acetate. At concentrations in the range 1.0—0.25 mol dm^{-3} the chemical shift varies little, increasing in field from $-1\,337$ to $-1\,429$ p.p.m., but at concentrations of less than 0.1 mol dm^{-3} the shift moves more rapidly to higher field, reaching a value of $-1\,956$ p.p.m. at a concentration of 0.01 mol dm^{-3}. These observations are readily interpreted in terms of the ionisation equilibrium (6). Computer simulation

$$Pb(O_2CCH_3)_2(H_2O)_p \rightleftharpoons [Pb(O_2CCH_3)(H_2O)_q]^+ + O_2CCH_3^- \quad (6)$$

of this rapidly exchanging system yields a value of 0.0139(1) mol dm^{-3} for the dissociation constant, $K_{dissoc.} = [Pb(O_2CCH_3)_2(H_2O)_q{}^+][O_2CCH_3{}^-]/[Pb(O_2CCH_3)_2(H_2O)_p]$ at 25 °C, and calculated values of $-1\,202(3)$ and $-2\,299$ (5) p.p.m. for the neutral $Pb(O_2CCH_3)_2(H_2O)_p$ and cationic $[Pb(O_2CCH_3)(H_2O)_q]^+$ species, respectively. The hydrated lead(II) cation does not participate in the equilibrium under the present experimental conditions, and only occurs at very much lower concentrations (*ca.* 10^{-6} mol dm^{-3}).

Table 2. Dissociation constants ($K_{dissoc.}$) and calculated lead-207 chemical shift values for $Pb(O_2CCH_3)_2$ and $[Pb(O_2CCH_3)]^+$ at various temperatures

T/K	δ(Pb^1) [a]/ p.p.m.	δ(Pb^2) [b]/ p.p.m.	$10^2K_{dissoc.}$/ mol dm^{-3}
303	−2 410	−1 175	1.356(7)
309	−2 435	−1 162	1.227(7)
313	−2 460	−1 151	1.073(6)
319	−2 480	−1 139.5	0.989(5)
323	−2 484	−1 133	0.916(5)

[a] $Pb^1 = [Pb(O_2CCH_3)]^+$. [b] $Pb^2 = Pb(O_2CCH_3)_2$.

The vast difference in chemical shift between the two equilibrating species indicates a quite different electronic structure for each. The resonance position for the monoacetatolead(II) monocation ($-2\,299$ p.p.m.) suggests a structure similar to that of the hydrated lead(II) and nitratolead(II) cations, with the lone pair again confined to the metal 6*s* orbital. The rather less electronegative acetato-group now bonds with more covalent character to lead, giving rise to the higher chemical shift. In the solid, lead(II) acetate trihydrate possesses a chain structure with chelating and bridging acetato-groups together with co-ordinated water, raising the co-ordination number at lead(II) to eight.[6] In spite of this high co-ordination number, an apparent vacancy in the co-ordination sphere suggests stereochemical activity for the metal lone pair. Persistence of such lone-pair stereoactivity for the neutral diacetatolead(II) solution species would readily rationalise its much lower-field chemical shift, since removal of lone-pair electron density from the isotropic 6*s* orbital into a hybrid *sp*^{3}*d*^{n} orbital would significantly reduce the nuclear shielding.

Figure 2 shows plots of lead-207 chemical shift *versus* lead(II) concentration for five other temperatures in the range 303—323 K, and in Table 2 are summarised the computed dissociation constants, K_{dissoc}, as well as the calculated values of δ(Pb^1) and δ(Pb^2). δ(Pb^2) is observed to move to higher field on increase in temperature, whilst simultaneously δ(Pb^1) moves to lower field, indicating minor changes in electronic structure for the two species with change in temperature, which may be ascribed to ligand reorientation and/or changes in the degree of solvation. The dissociation constant, $K_{dissoc.}$ decreases steadily from 1.36×10^{-2} mol dm^{-3} at 303 K to 0.92×10^{-2} mol dm^{-3} at 323 K. Thus, as the temperature increases, the degree of ionisation is reduced. The Arrhenius plot of ln $K_{dissoc.}$ *versus* 1/*T* is linear Figure 3 (six data points, slope = 1 709.4, intercept = −9.974, correlation coefficient = 0.983). From the evaluated enthalpy and free-energy changes, $\Delta H_{298} = -14.2$ kJ mol^{-1} and $\Delta G_{298} = 10.5$ kJ mol^{-1}, the entropy change during the process may be calculated to be −82.95 J K^{-1} mol^{-1}. Thus, although the un-ionised species is thermodynamically more stable, the ionisation process is favourable due to the negative entropy change. This we ascribe to an ion-solvation effect which localises a significantly larger number of water molecules than in the un-ionised species. As the temperature increases the effect becomes less pronounced.

$Pb(O_2CC_6F_5)_2$–thf.—Lead(II) pentafluorobenzoate is insoluble in water, but dissolves in thf, a 0.3 mol dm^{-3} solution

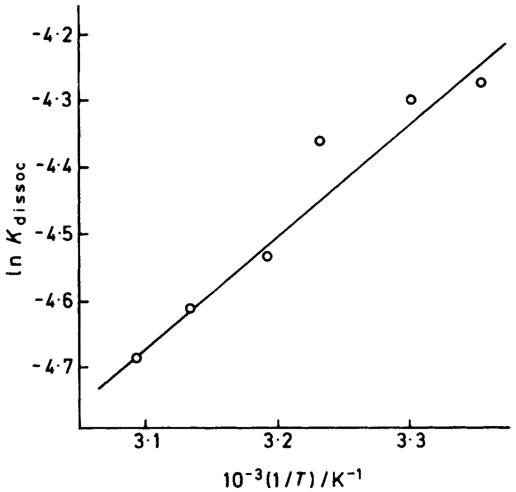

Figure 3. Plot of ln $K_{dissoc.}$ *versus* $1/T$

exhibiting a chemical shift of −1 258 p.p.m., decreasing to −959 p.p.m. at 0.06 mol dm^{-3}. Such chemical shift values are again characteristic of covalently bound carboxylatolead(II) species, with a stereochemically active lone pair. In the crystal, the bis(methanol) solvate possesses a chain structure with chelating and bridging carboxylate groups and co-ordinated methanol raising the co-ordination number to eight.[6] As with lead(II) acetate trihydrate, a vacancy in the co-ordination sphere indicates lone-pair stereoactivity. Since an equilibrium between solvated and unsolvated $Pb(O_2CC_6F_5)_2$ molecules would lead to a constant chemical shift value, the progressive increase in chemical shift on dilution has been interpreted in terms of a monomer–dimer equilibrium (3) in which both are presumably solvated to achieve co-ordination saturation and the monomer predominates at lower concentrations. Analysis of the data yields a value of 0.143(1) mol dm^{-3} for the dissociation constant, $K_{dissoc.} = [Pb(O_2CC_6F_5)_2]^2/[\{Pb(O_2CC_6F_5)_2\}_2]$, with calculated values of −1 882(10) and −677(4) p.p.m. for the dimer and monomer species, respectively.

$Pb[S_2P(OR)_2]_2$ (R = Et *or* Bu^i)-thf.—Tetrahydrofuran solutions of both lead(II) *O*,*O*′-dialkyl dithiophosphoridates exhibit an almost constant chemical shift of *ca.* −420 p.p.m. in the concentration range 0—1 mol dm^{-3}, consistent with the presence of strongly saturated $Pb[S_2P(OR)_2]_2$·thf molecules, analogous to the pyridine solvate of the lead(II) dithiocarbonate, $Pb(S_2COC_3H_7)_2 \cdot C_5H_5N$. Crystals of the latter compound contain isolated molecules in which the pyridine is directly bonded to the metal and the lone pair is stereoactive.[11]

$Pb[S_2P(OR)_2]_2$ (R = Et *or* Bu^i)-CH_2Cl_2.—In contrast to the behaviour in thf solution, the chemical shift of lead(II) *O*,*O*′-diethyl dithiophosphoridate in dichloromethane solution varies with concentration, moving steadily to lower field from the value of −310 p.p.m. observed for a 1 mol dm^{-3} solution. Since the isopropyl homologue, $Pb[S_2P(OPr^i)_2]_2$, is known to associate in the solid as well as exhibiting lone-pair stereoactivity,[12] the variation of chemical shift is interpreted, as in the $Pb(O_2CC_6F_5)_2$–thf system, in terms of a monomer–dimer equilibrium (4). Analysis of the data in terms of this equilibrium yields a value of 0.268(6) mol dm^{-3} for the dissociation constant $K_{dissoc.} = [Pb\{S_2P(OEt)_2\}_2]^2/[\{Pb[S_2P(OEt)_2]_2\}_2]$ with calculated values of +107(2) and −592(6) p.p.m. for the monomer and dimer species, respectively. The difference in behaviour in dichloromethane is ascribed to the lack of donor ability of this solvent compared with the strongly donating thf, and so the lead(II) dithiophosphoridate prefers to associate. The few data obtained for $Pb[S_2P(OBu^i)_2]_2$ show that it behaves in a similar fashion.

Conclusions

It is apparent from the data that there is a strong correlation between the lead-207 chemical shift and the electronic structure of the species present in solution. Species in which the lone pair of electrons is confined to the lead 6*s* orbital are characterised by very high-field shifts resulting from efficient nuclear shielding. For more covalently bound ligands, the lone pair is stereochemically active in a hybrid sp^3d^n orbital, and hence the shielding is significantly weaker and the chemical shifts are at much lower fields.

References

1 J. D. Kennedy, W. McFarlane, and G. S. Pyne, *J. Chem. Soc., Dalton Trans.*, 1977, 2332.
2 T. N. Mitchell, J. Gmehling, and F. Huber, *J. Chem. Soc., Dalton Trans.*, 1978, 960.
3 J. D. Kennedy, W. McFarlane, G. S. Pyne, and B. Wrackmeyer, *J. Organomet. Chem.*, 1980, **195**, 285.
4 M. J. Cooper, A. K. Holliday, P. H. Makin, R. J. Puddephatt, and P. J. Smith, *J. Organomet. Chem.*, 1974, **65**, 377.
5 R. N. Sylva and P. L. Brown, *J. Chem. Soc., Dalton Trans.*, 1980, 1577 and refs. therein.
6 P. G. Harrison and A. T. Steel, *J. Organomet. Chem.*, 1982, **239**, 105.
7 M. Vijayan and M. A. Viswamitra, *Acta Crystallogr.*, 1966, **21**, 522.
8 G. E. Maciel and J. L. Dallas, *J. Am. Chem. Soc.*, 1973, **95**, 2039.
9 G. H. Nancollas, *J. Chem. Soc.*, 1955, 1458.
10 H. M. Hershenson, M. E. Smith, and D. N. Hume, *J. Am. Chem. Soc.*, 1953, **75**, 507.
11 H. Hagihara, N. Yoshida, and Y. Watanabe, *Acta Crystallogr., Sect. B*, 1969, **25**, 1775.
12 T. Ito, *Acta Crystallogr., Sect. B*, 1972, **28**, 1034.

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