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Lead(II) nitrate and hexafluorosilicate complexes with neutral diphosphine coordination†

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Rare examples of phosphine complexes of lead(II) are reported. The reaction of $\text{Pb}(\text{NO}_3)_2$ with $\text{Me}_2\text{P}(\text{CH}_2)_2\text{PMe}_2$, $o\text{-C}_6\text{H}_4(\text{PMe}_2)_2$ or $\text{Et}_2\text{P}(\text{CH}_2)_2\text{PEt}_2$ (L–L) in $\text{H}_2\text{O}/\text{MeCN}$ gave white $[\text{Pb}(\text{L}-\text{L})(\text{NO}_3)_2]$, irrespective of the ratio of reagents used. The X-ray structures of $[\text{Pb}\{\text{Me}_2\text{P}(\text{CH}_2)_2\text{PMe}_2\}(\text{NO}_3)_2]$ and $[\text{Pb}\{o\text{-C}_6\text{H}_4(\text{PMe}_2)_2\}(\text{NO}_3)_2]$ reveal chelating diphosphines and $\kappa^2\text{-NO}_3^-$ groups occupying one hemisphere about the lead centre with single oxygen bridges to two further nitrate groups from neighbouring molecules completing a distorted eight-coordinate geometry. Using $\text{Pb}(\text{SiF}_6)\cdot 2\text{H}_2\text{O}$ produced $[\text{Pb}\{o\text{-C}_6\text{H}_4(\text{PMe}_2)_2\}(\text{H}_2\text{O})(\text{SiF}_6)]\cdot \text{H}_2\text{O}$ which has a chelating diphosphine, the water molecule and a coordinated SiF_6^{2-} group (which could be described as either $\kappa^1\text{-}$ or asymmetric $\kappa^3\text{-}$ coordinated to the lead), with further Pb–F interactions to neighbouring molecules producing a chain polymer structure. The structure of $[\text{Pb}\{o\text{-C}_6\text{H}_4(\text{PMe}_2)_2\}(\text{DMF})_2(\text{SiF}_6)]\cdot \text{DMF}$ was also determined and contains dimers with fluorosilicate bridges. Adventitious oxygen readily form diphosphine dioxide complexes, and the structures of $[\text{Pb}\{\text{Et}_2(\text{O})\text{P}(\text{CH}_2)_2\text{P}(\text{O})\text{Et}_2\}_2(\text{NO}_3)_2]$ and $[\text{Pb}\{\text{Me}_2\text{P}(\text{CH}_2)_2\text{PMe}_2\}\{\text{Me}_2(\text{O})\text{P}(\text{CH}_2)_2\text{P}(\text{O})\text{Me}_2\}][\text{BF}_4]_2\cdot \frac{1}{2}\text{MeNO}_2$ produced in this way were determined. The former contains eight-coordinate lead with $\kappa^2\text{-NO}_3^-$ groups and bridging diphosphine dioxides, which results in an infinite polymer. In the latter the diphosphine is chelated but the diphosphine dioxide bridges between Pb(II) centres, with coordinated BF_4^- groups completing a very distorted ten-coordinate moiety. Attempts to isolate similar complexes with $o\text{-C}_6\text{H}_4(\text{PPh}_2)_2$ or $o\text{-C}_6\text{H}_4(\text{AsMe}_2)_2$ were unsuccessful.

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Introduction

Classed as an intermediate Lewis acid by Pearson's hard and soft acid–base concept,¹ lead(II) forms stable complexes with a broad range of neutral and charged donor ligands across Groups 14–17.^{2–4} Although the majority of complexes are with hard (oxygen and nitrogen) donor atom ligands,³ there is also considerable coordination chemistry with softer sulfur and selenium donor ligands.⁴ However, whilst phosphine complexes of most heavy main group metals (including Hg(II), In(III), Sn(II), Sn(IV) and Bi(III)) are well established,⁵ the coordination chemistry of lead(II) with neutral phosphines is extremely limited.⁵ While $[\text{Pb}\{\text{Et}_2\text{P}(\text{CH}_2)_2\text{PEt}_2\}_2\text{Br}_2]$ and $[\text{Pb}\{\text{Et}_2\text{P}(\text{CH}_2)_2\text{PEt}_2\}_2(\text{ClO}_4)_2]$ were claimed in 1960, characterisation was limited to partial microanalysis,⁶ and the only structurally characterised examples of neutral diphosphine complexes are the lead(II) thiolates $[(2,6\text{-Me}_2\text{C}_6\text{H}_3\text{S})_2\text{Pb}]_2\{\mu\text{-Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}_2\}$ and $[(2,6\text{-Me}_2\text{C}_6\text{H}_3\text{S})_2\text{Pb}]_3\{\text{Me}_2\text{P}(\text{CH}_2)_2\text{PMe}_2\}$.⁷ The latter contains a chain of the three lead centres linked by thiolate

bridges, with the $\text{Me}_2\text{P}(\text{CH}_2)_2\text{PMe}_2$ chelating to the central Pb.⁷ Several 1:1 polydentate phosphine complexes of $\text{Pb}(\text{SbF}_6)_2$ have also been studied by *in situ* $^{31}\text{P}\{^1\text{H}\}$ and ^{207}Pb NMR spectroscopy in MeNO_2 , although no complexes were isolated.^{8,9}

One of the major challenges in synthesising lead(II) complexes with neutral diphosphine ligands is in finding a suitable lead precursor. Main group phosphine coordination chemistry has mostly been performed with metal halides,⁵ but the insoluble and intractable nature of the lead dihalides precludes easy synthetic access to this area; instead lead(II) oxo-salts such as acetate, nitrate or perchlorate are often used.^{2,3} Previously we have investigated crown ether, oxathia- and oxaseleno-macrocyclic complexes of $\text{Pb}(\text{NO}_3)_2$, $\text{Pb}(\text{BF}_4)_2$ and $\text{Pb}(\text{PF}_6)_2$, finding that the weakly coordinating fluoroanions also readily enter the first coordination sphere of the lead.¹⁰ The very stable di- and tri-imine complexes of Pb(II) with $\text{Pb}(\text{NO}_3)_2$ or $\text{Pb}(\text{ClO}_4)_2$ exhibit high coordination numbers and irregular geometries,¹¹ whilst complexes of these ligands with $\text{Pb}(\text{BF}_4)_2$ and $\text{Pb}(\text{SiF}_6)$ were shown to exhibit a variety of different fluoroanion coordination modes.¹² Here we report the reactions of $\text{Pb}(\text{NO}_3)_2$, $\text{Pb}(\text{SiF}_6)$ and $\text{Pb}(\text{BF}_4)_2$ with the diphosphines $o\text{-C}_6\text{H}_4(\text{PMe}_2)_2$, $\text{Me}_2\text{P}(\text{CH}_2)_2\text{PMe}_2$ and $\text{Et}_2\text{P}(\text{CH}_2)_2\text{PEt}_2$, focussing on the coordination behaviour of both the diphosphine and

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counterion in the complexes formed. Lead is a large metal centre with a covalent radius of 1.46 Å and hence regularly forms complexes with high coordination numbers where the geometry is governed by the number and steric demands of the ligands present, as well as by inter-ligand repulsions. The presence of a formal lone pair on lead(II) will also have an effect on the geometry observed if it is stereochemically active.^{2,3}

Experimental section

All preparations were carried out under a dry dinitrogen atmosphere using standard Schlenk and glove-box techniques. Lead(II) nitrate and lead(II) tetrafluoroborate (the latter as 50% solutions in water) were obtained from Aldrich and used as received. Lead(II) hexafluorosilicate dihydrate was obtained from Alfa Aesar and used as received. Aqueous solutions of the lead salts were degassed before use, by bubbling with N₂. The ligands were obtained commercially, (Strem) apart from *o*-C₆H₄(PMe₂)₂ and *o*-C₆H₄(AsMe₂)₂ which were made by the literature methods.¹³ Solvents were dried by distillation from CaH₂ (CH₂Cl₂, CH₃CN) or sodium benzophenone ketyl (hexane, Et₂O). IR spectra were recorded as Nujol mulls between CsI plates using a Perkin Elmer Spectrum 100 spectrometer over the range 4000–200 cm⁻¹. ¹H and ³¹P-{¹H} NMR spectra were recorded using a Bruker AV300 or DPX400 spectrometer and referenced to the residual solvent resonance and external 85% H₃PO₄ respectively. Microanalytical measurements were performed by London Metropolitan University.

[Pb{*o*-C₆H₄(PMe₂)₂}(NO₃)₂]

To *o*-C₆H₄(PMe₂)₂ (0.090 g, 0.45 mmol) in CH₃CN (5 mL) was added a degassed solution of Pb(NO₃)₂ (0.150 g, 0.45 mmol) in deionised water (3 mL). A white precipitate formed rapidly on stirring; the reaction was stirred for 2 h, then the white powder was isolated by filtration and dried *in vacuo*. Yield: 0.056 g, 23%. Anal. Calc. for C₁₀H₁₆N₂O₆P₂Pb: (529.4) C, 22.7; H, 3.1; N, 5.3. Found: C, 22.6; H, 3.1; N, 5.2%. IR (Nujol): $\nu = 1314$ (s), 1295 (s), 1033 (s), 837 (sh), 818 (m) (NO₃) cm⁻¹.

[Pb{Me₂P(CH₂)₂PMe₂}(NO₃)₂]

To Me₂P(CH₂)₂PMe₂ (0.091 g, 0.60 mmol) in CH₃CN (5 mL) was added a degassed solution of Pb(NO₃)₂ (0.101 g, 0.30 mmol) in deionised water (5 mL), giving a colourless solution. The reaction was stirred for 1 h, then the solvent was concentrated *in vacuo* and the resulting white powder was filtered and dried *in vacuo*. Yield: 0.071 g, 48% based on Pb. Anal. Calc. for C₆H₁₆N₂O₆P₂Pb: (481.4) C, 15.0; H, 3.4; N, 5.8. Found: C, 15.1; H, 3.3; N, 5.8%. IR (Nujol): $\nu = 1310$ (vs, br), 1038 (s), 840 (w), 819 (m) (NO₃) cm⁻¹.

[Pb{Et₂P(CH₂)₂PEt₂}(NO₃)₂]

To a degassed solution of Pb(NO₃)₂ (0.162 g, 0.49 mmol) in deionised water (3 mL) was added Et₂P(CH₂)₂PEt₂ (0.101 g, 0.49 mmol) in CH₃CN (5 mL) to give a colourless solution. The

reaction was stirred for 2 h, then the solvent volume was reduced to about 3 mL *in vacuo*. The resulting white precipitate was isolated by filtration and dried *in vacuo* to give a white powder. Yield: 0.092 g, 35%. Anal. Calc. for C₁₀H₂₄N₂O₆P₂Pb: (537.5) C, 22.4; H, 4.5; N, 5.2. Found: C, 22.2; H, 4.6; N, 5.2%. ¹H NMR (CD₂Cl₂, 295 K): $\delta = 1.19$ – 1.27 (m, [12H], CH₃), 1.92– 2.02 (m, [4H], CH₂), 2.20– 2.35 (m, [4H], CH₂), 2.40 (d, [4H], CH₂). ³¹P{¹H} NMR (CH₂Cl₂/CD₂Cl₂, 295 K): $\delta = 89.3$ (s); (223 K): 89.5 (s, ¹J_{PPb} = 2465 Hz); (193 K): 89.6 (s, ¹J_{PPb} = 2532 Hz). IR (Nujol): $\nu = 1300$ (s, br), 1029 (s), 816 (m) (NO₃) cm⁻¹. Small colourless single crystals of the phosphine oxide complex, [Pb{Et₂(O)P(CH₂)₂P(O)Et₂}(NO₃)₂], were grown from layering hexane onto a solution of the isolated powder dissolved in the minimal amount of CH₂Cl₂.

[Pb{*o*-C₆H₄(PMe₂)₂}(H₂O)(SiF₆)·H₂O]

To a degassed solution of Pb(SiF₆)·2H₂O (0.151 g, 0.39 mmol) in deionised water (10 mL) was added *o*-C₆H₄(PMe₂)₂ (0.077 g, 0.39 mmol) in CH₃CN (5 mL) which caused the precipitation of a small amount of white solid. The reaction was stirred for 1.5 h, then the solid was removed by filtration to leave a colourless solution. The solvent was removed *in vacuo* and the resulting white powder was dried *in vacuo*. Yield: 0.110 g, 48%. IR (Nujol): $\nu = 3500$ (br), 1628 (m, br) (H₂O), 721 (vs, br), 473 (s), 446 (s) (SiF₆) cm⁻¹. Small colourless single crystals of [Pb{*o*-C₆H₄(PMe₂)₂}(H₂O)(SiF₆)·H₂O] were grown by layering Et₂O onto a solution of the isolated product dissolved in the minimal amount of DMF.

In a similar reaction where the *o*-C₆H₄(PMe₂)₂ to Pb(SiF₆)·2H₂O ratio used was 2 : 1.

[Pb{Me₂P(CH₂)₂PMe₂}{Me₂(O)P(CH₂)₂P(O)Me₂}[BF₄]₂·¹/₂MeNO₂]

To a degassed solution of Me₂P(CH₂)₂PMe₂ (0.087 g, 0.58 mmol) in MeNO₂ (6 mL) was added Pb(BF₄)₂ as a 50% aqueous solution (0.229 g, 0.30 mmol) that had been degassed (bubbling with N₂) beforehand. A small amount of white precipitate rapidly formed, which was removed by filtration, then Et₂O (10 mL) was layered onto the colourless filtrate, giving a few small colourless crystals.

X-Ray experimental

Details of the crystallographic data collection and refinement parameters are given in Table 1. Crystals suitable for single crystal X-ray analysis were obtained as described above. Data collections used a Rigaku AFC12 goniometer equipped with an enhanced sensitivity (HG) Saturn724+ detector mounted at the window of an FR-E+ SuperBright molybdenum ($\lambda = 0.71073$ Å) rotating anode generator with VHF Varimax optics (70 micron focus) with the crystal held at 100 K (N₂ cryostream). Structure solution and refinements were performed with SHELX-(S/L)97¹⁴ and were straightforward, except where detailed below. H atoms bonded to C were placed in calculated positions using the default C–H distance and refined using a riding model. Attempts to improve the absorption correction for both [Pb{*o*-C₆H₄(PMe₂)₂}(NO₃)₂] and [Pb{Me₂P(CH₂)₂PMe₂}(NO₃)₂] failed to eliminate the large residual density electron peaks <1 Å



Table 1 Crystal data and structural refinement details^a

| Compound | [Pb(Me ₂ P(CH ₂) ₂ PMe ₂) ₂] ²⁻ PMe ₂ (NO ₃) ₂ | [Pb(Me ₂ P(CH ₂) ₂ PMe ₂) ₂] ²⁻ P(O)Et ₂ (NO ₃) ₂ | [Pb(o-C ₆ H ₄ (PMe ₂) ₂) ₂] ²⁻ (DMF) ₂ (SiF ₆) ₂ ·H ₂ O | [Pb(Me ₂ P(CH ₂) ₂ PMe ₂) ₂] ²⁻ P(O)Me ₂ (BF ₄) ₂ · $\frac{1}{2}$ MeNO ₂ |
|---|--|---|--|---|
| Formula | C ₆ H ₁₆ N ₂ O ₆ P ₂ Pb | C ₂₀ H ₄₈ N ₂ O ₁₀ P ₄ Pb | C ₁₀ H ₂₀ F ₆ O ₂ P ₂ PbSi | C _{12.50} H _{33.50} B ₂ F ₈ N _{0.50} O ₃ P ₄ Pb |
| <i>M</i> | 481.34 | 807.67 | 583.48 | 743.59 |
| Crystal system | Monoclinic | Monoclinic | Triclinic | Orthorhombic |
| Space group (no.) | <i>P</i> 2 ₁ / <i>n</i> (no. 14) | <i>P</i> 2 ₁ / <i>c</i> (no. 14) | <i>P</i> 1 (no. 2) | <i>F</i> ddd (no. 70) |
| <i>a</i> /Å | 10.182(4) | 15.1483(5) | 6.6164(17) | 16.938(6) |
| <i>b</i> /Å | 10.863(3) | 13.8900(4) | 10.637(3) | 24.212(9) |
| <i>c</i> /Å | 14.771(5) | 16.2854(5) | 12.354(3) | 25.686(10) |
| α /° | 90 | 90 | 93.580(6) | 90 |
| β /° | 91.614(5) | 112.383(3) | 93.952(3) | 90 |
| γ /° | 90 | 90 | 100.854(6) | 90 |
| <i>U</i> /Å ³ | 1633.0(9) | 3168.44(17) | 849.4(4) | 10 534(7) |
| <i>Z</i> | 4 | 4 | 2 | 16 |
| <i>V</i> (Mo-K α)/mm ⁻³ | 10.552 | 5.576 | 10.250 | 6.719 |
| <i>F</i> (000) | 1000 | 1616 | 552 | 5760 |
| Total no. reflns | 7115 | 26 042 | 7661 | 11 501 |
| <i>R</i> _{int} | 0.050 | 0.040 | 0.035 | 0.028 |
| Unique reflns | 3709 | 7234 | 3848 | 3021 |
| No. of params, restraints | 188, 0 | 342, 0 | 219, 2 | 212, 223 |
| <i>R</i> ₁ , <i>wR</i> ₂ [<i>I</i> > 2 σ (<i>I</i>)] ^b | 0.043, 0.101 | 0.031, 0.067 | 0.026, 0.064 | 0.053, 0.103 |
| <i>R</i> ₁ , <i>wR</i> ₂ (all data) | 0.052, 0.104 | 0.045, 0.073 | 0.028, 0.065 | 0.061, 0.108 |

^a Common items: *T* = 100 K; wavelength (Mo-K α) = 0.71073 Å; θ (max) = 27.5°; *R*₁ = $\sum ||F_o| - |F_c|| / \sum |F_o|$; *wR*₂ = $[\sum w(F_o^2 - F_c^2)^2 / \sum wF_o^2]^{1/2}$.

from Pb1. DFIX restraints were applied to the O–H distances of the lattice H₂O in [Pb{o-C₆H₄(PMe₂)₂}(H₂O)(SiF₆)]·H₂O. For [Pb{Me₂P(CH₂)₂PMe₂}(Me₂(O)P(CH₂)₂P(O)Me₂)] [BF₄]₂· $\frac{1}{2}$ MeNO₂ the BF₄⁻ anion was modelled as two distinct orientations (A and B) and DFIX restraints were applied to the B–F distances. The proportions of A and B were allowed to vary through FVAR2. The disorder in the methyl groups around P2 was satisfactorily modelled by splitting C5 and C6 into A and B sites, then applying DFIX restraints to the P–C distances. The proportions of A and B were allowed to vary through FVAR3 while isotropic restraints were used on C5A, C6A and C6B to maintain reasonable ellipsoids. The N1 of the fractionally occupied lattice MeNO₂ is located on a site with 222 symmetry giving a very disordered molecule. DFIX restraints were applied to the N–C and N–O distances.

Crystallographic data in cif format have been deposited with the Cambridge Crystallographic Data Centre (CCDC) and given numbers 1060048–1060053.

Results and discussion

The lead(II) salts used for the syntheses were Pb(NO₃)₂ and Pb(SiF₆)·2H₂O, both of which have negligible solubility in organic solvents that are commonly used for phosphine coordination chemistry, such as CH₂Cl₂ or toluene. Reactions were therefore performed by dissolving Pb(NO₃)₂ or Pb(SiF₆)·2H₂O in the minimum amount of water that had been purged with N₂ beforehand, to which a solution of the relevant diphosphine in MeCN was added, affording white powders. Owing to the insolubility of most of the complexes in common NMR solvents (CD₂Cl₂, CD₃CN, D₂O and CD₃OD), and the labile nature of Pb(II) in solution, the investigations have been driven by solid state characterisation, the key technique being single crystal X-ray diffraction, supported by identification of the anion using infrared spectroscopy, with elemental analysis to confirm the stoichiometries of the bulk samples. Crystals were typically grown by carefully layering a miscible solvent onto a solution of the pre-isolated complex as described in the Experimental. Of the isolated complexes only [Pb{Et₂P(CH₂)₂PET₂}(NO₃)₂] was sufficiently soluble in a weakly coordinating solvent (CD₂Cl₂) to allow multinuclear NMR studies. In donor solvents, the diphosphines were partially displaced and no useful data were obtained.

Lead(II) nitrate complexes

The reaction of Me₂P(CH₂)₂PMe₂ with Pb(NO₃)₂ in MeCN/H₂O formed only the 1 : 1 [Pb{Me₂P(CH₂)₂PMe₂}(NO₃)₂], despite a 2 : 1 molar ratio of reagents being used. Elemental analysis of the bulk powder isolated confirmed the 1 : 1 stoichiometry, while colourless crystals of [Pb{Me₂P(CH₂)₂PMe₂}(NO₃)₂] (Fig. 1a) were grown by layering Et₂O onto a DMF solution containing the complex. The structure shows the Me₂P(CH₂)₂PMe₂ ligand chelated symmetrically to the Pb(II) centre with *d*(Pb–P) = 2.7918(15) Å while the nitrate groups are asymmetrically κ^2 -coordinated (*d*(Pb–O) = 2.621(4), 2.859(5) Å), all on one hemi-



sphere of the lead. Two further Pb–O contacts, 2.995(4) Å, well within the Van der Waals radii sum of 3.54 Å for Pb...O¹⁵ from nitrates on neighbouring molecules link the units into an infinite polymer network (Fig. 1b) where the coordination number around the lead(II) centre is eight. The Pb–P bonds are ~0.05 Å shorter than those in [(2,6-Me₂C₆H₃S)₂Pb]₃{Me₂P(CH₂)₂PMe₂} (2.8389(10) Å).⁷

Similarly, [Pb{o-C₆H₄(PMe₂)₂}(NO₃)₂] was isolated as a white powder from a 1 : 1 mol. ratio reaction of *o*-C₆H₄(PMe₂)₂ with Pb(NO₃)₂. Colourless crystals were obtained from a DMF solution layered with Et₂O. A crystal structure determination revealed a similar molecular unit (Fig. 2a) to [Pb{Me₂P(CH₂)₂PMe₂}(NO₃)₂] with the lead(II) centre being eight coordi-

nate. Though no longer symmetrical the Pb–P bond lengths are comparable, while the O–Pb–O angle formed by the nitrate oxygen atoms nearest to the diposphine is larger in [Pb{o-C₆H₄(PMe₂)₂}(NO₃)₂] (147.36(16)° vs. 139.98(19)°). Again the third oxygen of the nitrate groups bridge (*d*(Pb–O) = 2.948(5), 2.959(5) Å) to neighbouring molecules to give an infinite chain structure (Fig. 2b).

The crystallographically identified κ²-coordinated nitrate groups can also be seen in the IR spectra of [Pb{Me₂P(CH₂)₂PMe₂}(NO₃)₂] and [Pb{o-C₆H₄(PMe₂)₂}(NO₃)₂]. The approximate C_{2v} symmetry of κ²-NO₃ groups means three IR active stretching modes (2A₁ + B₂) are expected;¹⁶ as seen with macrocyclic complexes of Pb(NO₃)₂ (e.g. [Pb(18-crown-6)-(NO₃)₂]), which also exhibit high coordination numbers and κ²-NO₃ groups, two stretches are observed at ~1310 and 1030 cm⁻¹ (the stretch anticipated at ~1470 cm⁻¹ is obscured by Nujol).¹⁰ A bending mode is also evident at ~815 cm⁻¹.¹⁶ Splitting of some of the bands was observed in the IR spec-

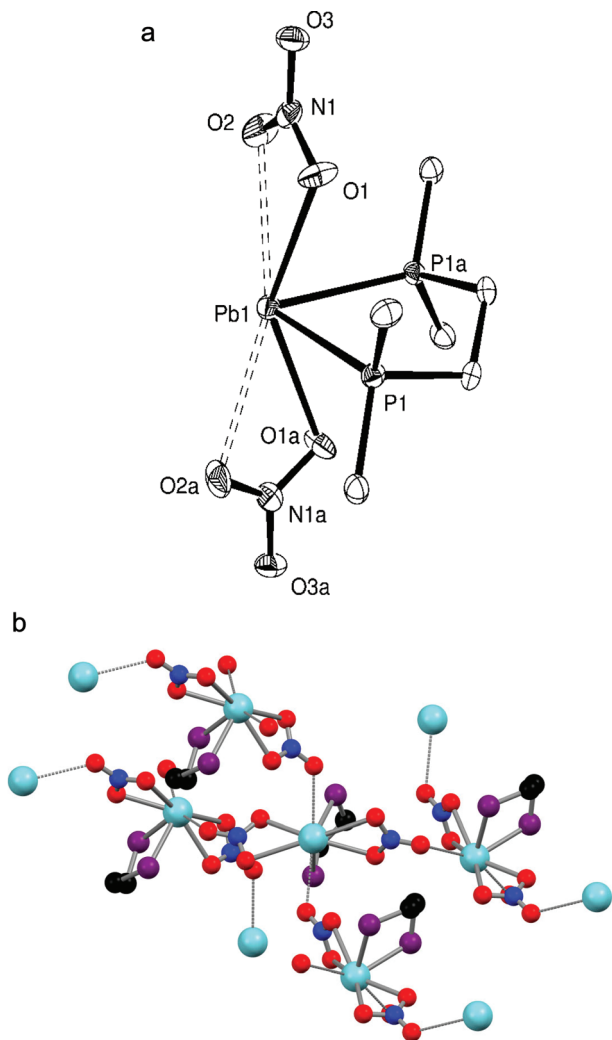


Fig. 1 (a) Crystal structure of [Pb{Me₂P(CH₂)₂PMe₂}(NO₃)₂] showing the atom labelling scheme. The displacement ellipsoids are drawn at the 50% probability level and H atoms are omitted for clarity. Symmetry operation: *a* = *x*, *y*, *-z*. Selected bond lengths (Å) and angles (°): Pb1–P1 = 2.7918(15), Pb1–O1 = 2.621(4), Pb1–O2 = 2.859(5), P1–Pb1–P1a = 74.19(6), O1–Pb1–O2 = 46.07(13), O1–Pb1–O1a = 139.98(19). (b) The extended structure of [Pb{Me₂P(CH₂)₂PMe₂}(NO₃)₂]. Methyl groups are omitted for clarity.

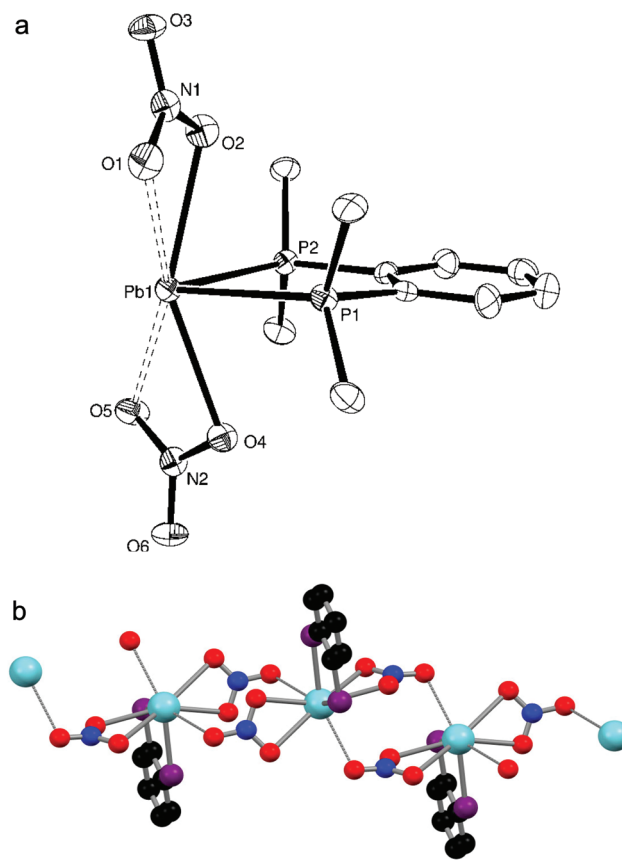


Fig. 2 (a) Crystal structure of [Pb{o-C₆H₄(PMe₂)₂}(NO₃)₂] showing the atom labelling scheme. The displacement ellipsoids are drawn at the 50% probability level and H atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Pb1–P1 = 2.806(2), Pb1–P2 = 2.8088(19), Pb1–O1 = 2.869(6), Pb1–O2 = 2.611(6), Pb1–O4 = 2.595(5), Pb1–O5 = 2.827(6), P1–Pb1–P2 = 71.95(6), O1–Pb1–O2 = 46.56(15), O2–Pb1–O4 = 147.37(16), O4–Pb1–O5 = 46.83(15). (b) The polymeric chain structure of [Pb{o-C₆H₄(PMe₂)₂}(NO₃)₂]. Methyl groups are omitted for clarity.



trum of $[\text{Pb}\{o\text{-C}_6\text{H}_4(\text{PMe}_2)_2\}(\text{NO}_3)_2]$, which is less clearly resolved for $[\text{Pb}\{\text{Me}_2\text{P}(\text{CH}_2)_2\text{PMe}_2\}(\text{NO}_3)_2]$.

Owing to the unpredictable geometries and the dissociative nature of complexes of Pb(II) in solution^{7,11} meaningful NMR spectra can generally only be obtained in non-competitive solvents such as CD_2Cl_2 , in which both $[\text{Pb}\{\text{Me}_2\text{P}(\text{CH}_2)_2\text{PMe}_2\}(\text{NO}_3)_2]$ and $[\text{Pb}\{o\text{-C}_6\text{H}_4(\text{PMe}_2)_2\}(\text{NO}_3)_2]$ were found to be insoluble. By using $\text{Et}_2\text{P}(\text{CH}_2)_2\text{PEt}_2$ as the ligand with $\text{Pb}(\text{NO}_3)_2$ under analogous conditions a white powder, $[\text{Pb}\{\text{Et}_2\text{P}(\text{CH}_2)_2\text{PEt}_2\}(\text{NO}_3)_2]$, was isolated which was found to be freely soluble in CD_2Cl_2 . There is a significant high frequency shift in the ^1H NMR spectrum of this complex confirming that the phosphine is coordinated, while a sharp singlet at $\delta = 89.3$ is observed in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum. This is a very large, high frequency shift from 'free' $\text{Et}_2\text{P}(\text{CH}_2)_2\text{PEt}_2$ ($\delta = -18$) whose magnitude is mirrored in the shifts seen by Dean *et al.*⁸ in their *in situ* NMR studies of phosphine complexes of $\text{Pb}(\text{SbF}_6)_2$. Upon cooling the solution to 223 K, ^{207}Pb satellites were observed, which sharpened upon further cooling to 193 K ($J_{\text{PbP}} = 2532$ Hz). The appearance of ^{207}Pb satellites only at low temperatures has been reported before in a study of Pb(II) complexes of 2-phosphinobenzenethiolates,¹⁷ and was attributed to ligand lability. Similarly, no resonances were observed in the ^{207}Pb NMR spectrum, even at low temperatures. To ensure that the resonances observed were indeed due to coordinated $\text{Et}_2\text{P}(\text{CH}_2)_2\text{PEt}_2$ (*i.e.* that no unwanted oxidation of the ligand had occurred), an NMR spectrum of the complex was taken in $\text{DMSO}-d_6$, which displaced the diphosphine and showed the resonance of the uncoordinated $\text{Et}_2\text{P}(\text{CH}_2)_2\text{PEt}_2$. Despite numerous attempts, no crystals of $[\text{Pb}\{\text{Et}_2\text{P}(\text{CH}_2)_2\text{PEt}_2\}(\text{NO}_3)_2]$ could be grown (instead a few crystals of the phosphine oxide complex $[\text{Pb}\{\text{Et}_2\text{P}(\text{O})(\text{CH}_2)_2\text{P}(\text{O})\text{Et}_2\}(\text{NO}_3)_2]$ were obtained, discussed below); the IR spectrum of $[\text{Pb}\{\text{Et}_2\text{P}(\text{CH}_2)_2\text{PEt}_2\}(\text{NO}_3)_2]$ indicates that the nitrate groups are again κ^2 -coordinated (bands at 1300, 1029 and 816 cm^{-1}), which when combined with the NMR spectroscopic evidence suggests that $[\text{Pb}\{\text{Et}_2\text{P}(\text{CH}_2)_2\text{PEt}_2\}(\text{NO}_3)_2]$ has a similar structure to the other bidentate phosphine complexes.

Although $[\text{Pb}\{\text{Me}_2\text{P}(\text{CH}_2)_2\text{PMe}_2\}(\text{NO}_3)_2]$ and $[\text{Pb}\{o\text{-C}_6\text{H}_4(\text{PMe}_2)_2\}(\text{NO}_3)_2]$ were found to dissolve completely in DMF, a property exploited in order to grow crystals of these complexes, its relatively strong coordinating nature makes it problematic for NMR studies of these dynamic and labile systems. For both complexes a single resonance was observed in $^{31}\text{P}\{^1\text{H}\}$ NMR spectra run in $\text{DMF}-d_7$, with chemical shifts intermediate between those expected by analogy with the complex $[\text{Pb}\{\text{Et}_2\text{P}(\text{CH}_2)_2\text{PEt}_2\}(\text{NO}_3)_2]$ and the uncoordinated ligand shifts. The chemical shifts varied widely with concentration, indicating partial displacement of the diphosphine and rapidly exchanging systems. The values are not quoted. $[\text{Pb}\{\text{Et}_2\text{P}(\text{CH}_2)_2\text{PEt}_2\}(\text{NO}_3)_2]$ was also found to be partially decomposed by $\text{DMF}-d_7$.

Under the same reaction conditions the weaker σ -donor and sterically more crowded ligand $o\text{-C}_6\text{H}_4(\text{PPh}_2)_2$ did not form a complex with $\text{Pb}(\text{NO}_3)_2$. No complex could be isolated with $o\text{-C}_6\text{H}_4(\text{AsMe}_2)_2$, suggesting that the alkylphosphines are

better donors in these systems than alkylarsines, an effect also observed with other Group 14 metal acceptors.⁵

Lead(II) hexafluorosilicate complexes

The reaction of $\text{Pb}(\text{SiF}_6)\cdot 2\text{H}_2\text{O}$ with $o\text{-C}_6\text{H}_4(\text{PMe}_2)_2$ in a 1:1 ratio yielded a white powder which, when dissolved in DMF and layered with Et_2O , gave small colourless crystals of $[\text{Pb}\{o\text{-C}_6\text{H}_4(\text{PMe}_2)_2\}(\text{H}_2\text{O})(\text{SiF}_6)]\cdot \text{H}_2\text{O}$. The crystal structure (Fig. 3a) shows the diphosphine to be asymmetrically chelating, with a short Pb–F bond ($d(\text{Pb1-F5}) = 2.573(3)\text{ \AA}$) to a κ^1 -coordinated SiF_6^{2-} group and a further bond to a water molecule, so that overall the core molecular geometry is very similar to that of $[\text{Pb}\{o\text{-C}_6\text{H}_4(\text{PMe}_2)_2\}(\text{NO}_3)_2]$ (Fig. 2a), although the disparity in Pb–P bond lengths is greater ($\sim 0.03\text{ \AA}$) and the F–Pb–O angle is large ($154.76(11)^\circ$). The core geometry is therefore little affected by the anion present, with the primary contacts again covering one hemisphere of the lead. Although two more Pb–F distances ($d(\text{Pb1-F1}) = 3.201(3)$, $d(\text{Pb1-F4}) = 3.167(3)\text{ \AA}$) lie well within the sum of the Van der Waal's radii of 3.49 \AA for $\text{Pb}\cdots\text{F}$,¹⁴ these long contacts are probably the result of packing within the crystal lattice causing these F atoms to lie close to the Pb(II) centre. Nevertheless, an alternative description for the molecular structure of $[\text{Pb}\{o\text{-C}_6\text{H}_4(\text{PMe}_2)_2\}(\text{H}_2\text{O})(\text{SiF}_6)]\cdot \text{H}_2\text{O}$ is that the SiF_6^{2-} group is asymmetrically κ^3 -coordinated. These units are arranged into infinite strands by a Pb–F interaction from a neighbouring SiF_6^{2-} group ($d(\text{Pb-F}) = 2.815(3)\text{ \AA}$); two further Pb–F interactions with a SiF_6^{2-} group on a parallel strand ($d(\text{Pb-F}) = 2.795(3)$, $3.083(3)\text{ \AA}$) gives a polymeric chain structure overall (Fig. 3b), where the lead(II) centre is seven coordinate (or nine if the core SiF_6^{2-} group is described as κ^3 -coordinated). The $o\text{-C}_6\text{H}_4(\text{PMe}_2)_2$ groups are arranged so that they point outwards from the chain. The coordinated water molecule is also hydrogen bonded to a lattice water molecule ($\text{HO-H}\cdots\text{OH}_2 = 1.89(7)\text{ \AA}$), and together these form a hydrogen-bonding network (Fig. 3b) with F atoms on nearby SiF_6^{2-} groups ($\text{HO-H}\cdots\text{F} = 1.93(2)$, $2.05(6)$, $2.14(3)\text{ \AA}$).

The IR spectrum of the bulk solid confirms the presence of the SiF_6^{2-} group, although the anion coordination mode cannot be reliably identified.¹⁶ The stretching mode is significantly broadened, indicating that the Pb–F interactions are too weak to lower the symmetry of the fluoroanion sufficiently to give resolved splittings.¹²¹ Water is also visible in the IR spectrum, indicating that the bulk solid is probably also $[\text{Pb}\{o\text{-C}_6\text{H}_4(\text{PMe}_2)_2\}(\text{H}_2\text{O})(\text{SiF}_6)]\cdot x\text{H}_2\text{O}$, though a satisfactory elemental analysis could not be obtained. Poor solubility precluded NMR analysis of this complex.

Repetition of the reaction with a 2:1 (diphosphine: Pb) ratio yielded a few crystals of $[\text{Pb}\{o\text{-C}_6\text{H}_4(\text{PMe}_2)_2\}(\text{DMF})_2(\text{SiF}_6)]\cdot \text{DMF}$, again demonstrating the preference of the Pb(II) centre to coordinate to just one diphosphine ligand. The asymmetric unit has the expected core bonding environment (P_2FO) around the lead, with an O-bonded DMF molecule in place of H_2O , giving a F–Pb–O angle of $140.82(12)^\circ$. The SiF_6^{2-} group is now κ^2 - or κ^3 -coordinated depending on the viewpoint – the $d(\text{Pb1-F3})$ is $\sim 0.3\text{ \AA}$ shorter than the comparable distance in $[\text{Pb}\{o\text{-C}_6\text{H}_4(\text{PMe}_2)_2\}(\text{H}_2\text{O})(\text{SiF}_6)]\cdot \text{H}_2\text{O}$, while the $d(\text{Pb1-F2})$



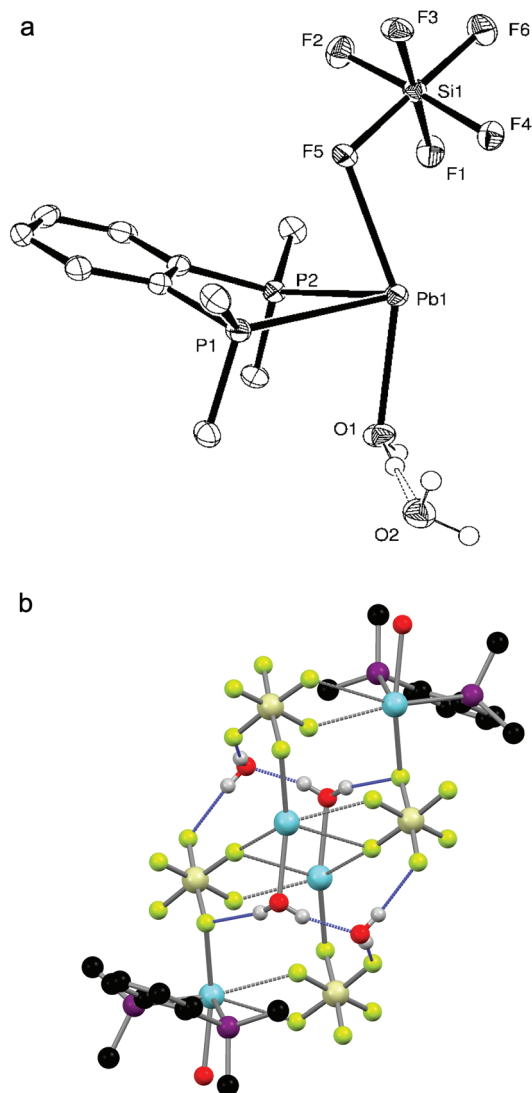


Fig. 3 (a) Crystal structure of $[\text{Pb}\{\text{o-C}_6\text{H}_4(\text{PMe}_2)_2\}(\text{H}_2\text{O})(\text{SiF}_6)]\cdot\text{H}_2\text{O}$ showing the atom labelling scheme. The displacement ellipsoids are drawn at the 50% probability level and H atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): $\text{Pb1-P1} = 2.8299(14)$, $\text{Pb1-P2} = 2.7976(13)$, $\text{Pb1-F5} = 2.573(3)$, $\text{Pb1-O1} = 2.496(3)$, $\text{P1-Pb1-P2} = 69.67(4)$, $\text{F5-Pb1-O1} = 154.76(11)$. (b) The polymeric chain structure of $[\text{Pb}\{\text{o-C}_6\text{H}_4(\text{PMe}_2)_2\}(\text{H}_2\text{O})(\text{SiF}_6)]\cdot\text{H}_2\text{O}$. The intermolecular H-bonding network is shown in blue and the diphosphines on the two central lead atoms are omitted for clarity.

remains long at $3.081(4)$ Å. The size of the DMF molecule and the lack of hydrogen bonding are presumably the main reasons the units now dimerise (Fig. 4) with the SiF_6^{2-} groups bridging *via* one F atom per fluoroanion. The orientation of a second DMF molecule close to the $\text{Pb}(\text{II})$ centre suggests that it is also interacting with the lead ($d(\text{Pb-O}) = 3.263(6)$ Å), which gives an overall coordination number of seven or eight for $\text{Pb}(\text{II})$. There is also a DMF solvate molecule in the structure. Formation of this complex also shows that DMF will readily coordinate to lead(II), highlighting its unsuitability as a NMR solvent in these systems, but because of the lability of the

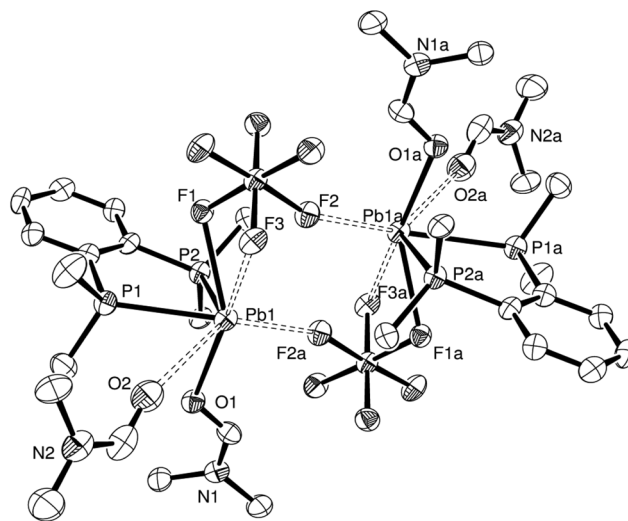


Fig. 4 Crystal structure of the SiF_6 -bridged dimer present in $[\text{Pb}\{\text{o-C}_6\text{H}_4(\text{PMe}_2)_2\}(\text{DMF})_2(\text{SiF}_6)]\cdot\text{DMF}$ showing the atom labelling scheme. The displacement ellipsoids are drawn at the 50% probability level. H atoms and DMF solvate molecules are omitted for clarity. Symmetry operation: $a = 2 - x, 2 - y, 1 - z$. Selected bond lengths (Å) and angles (°): $\text{Pb1-P1} = 2.7671(19)$, $\text{Pb1-P2} = 2.7553(16)$, $\text{Pb1-F1} = 2.585(3)$, $\text{Pb1-F3} = 2.894(3)$, $\text{Pb1-F2a} = 2.752(3)$, $\text{Pb1-O1} = 2.463(4)$, $\text{Pb1-O2} = 3.263(6)$, $\text{P1-Pb1-P2} = 72.30(5)$, $\text{F1-Pb1-F3} = 50.67(9)$, $\text{F1-Pb1-F2a} = 110.58(10)$, $\text{F1-Pb1-O1} = 140.82(12)$, $\text{F1-Pb1-O2} = 109.10(12)$.

complex in solution, the structure obtained is ultimately dependant on which complex crystallises out under the conditions employed.

Phosphine oxide complexes

When trying to grow crystals of $[\text{Pb}\{\text{Et}_2\text{P}(\text{CH}_2)_2\text{PET}_2\}(\text{NO}_3)_2]$ by recrystallisation from CH_2Cl_2 and *n*-hexane, a few small colourless crystals of $[\text{Pb}\{\text{Et}_2(\text{O})\text{P}(\text{CH}_2)_2\text{P}(\text{O})\text{Et}_2\}_2(\text{NO}_3)_2]$ were instead isolated, indicating that *in situ* oxidation of the ligand has occurred, presumably due to adventitious O_2 . The X-ray structure determination reveals (Fig. 5a) that the $\text{Et}_2(\text{O})\text{P}(\text{CH}_2)_2\text{P}(\text{O})\text{Et}_2$ ligands each bridge to different $\text{Pb}(\text{II})$ atoms, and that there are two phosphine oxide ligands per metal centre, despite the parent phosphine complex having a 1 : 1 stoichiometry. This gives a core PbO_4 geometry, with one Pb-O bond ~ 0.1 Å longer than the other three and a O1-Pb1-O4 angle of $160.29(9)^\circ$. Interactions with the nitrate groups are weaker than in $[\text{Pb}(\text{L-L})(\text{NO}_3)_2]$ ($\text{L-L} = \text{o-C}_6\text{H}_4(\text{PMe}_2)_2, \text{Me}_2\text{P}(\text{CH}_2)_2\text{PMe}_2$) but they remain κ^2 -coordinated (the third oxygen is uncoordinated) and fill the remainder of the coordination sphere, to give eight coordinate lead. Due to the bridging nature of the phosphine oxide groups, the extended structure (Fig. 5b) is an infinite polymer network.

The *in situ* oxidation of diphosphine ligands in the presence of heavy *p*-block metals has been reported before;⁵ for example, the oxidation of the 1 : 1 adduct of BiCl_3 and $\text{Ph}_2\text{PCH}_2\text{PPh}_2$ to the crystallographically identified $[\text{BiCl}_3\{\text{Ph}_2\text{P}(\text{O})\text{CH}_2\text{P}(\text{O})\text{Ph}_2\}]_2$ having occurred when trying to grow crystals



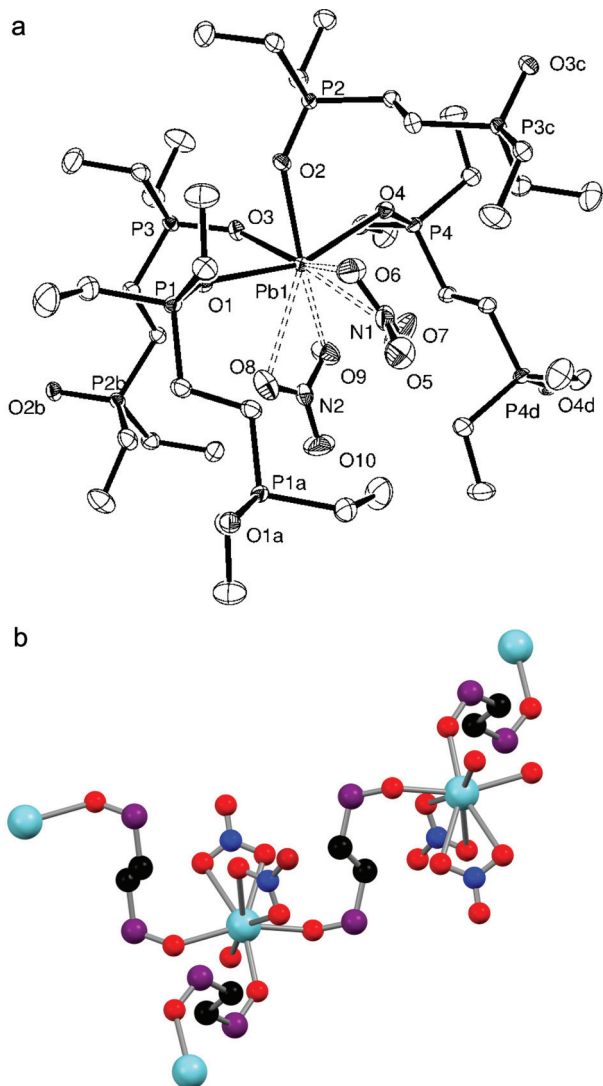


Fig. 5 (a) Crystal structure of $[\text{Pb}(\text{Et}_2(\text{O})\text{P}(\text{CH}_2)_2\text{P}(\text{O})\text{Et}_2)_2(\text{NO}_3)_2]$ showing the atom labelling scheme. The displacement ellipsoids are drawn at the 50% probability level and H atoms are omitted for clarity. Symmetry operations: $a = -x, 1 - y, 1 - z$; $b = x, 1/2 - y, 1/2 + z$; $c = x, 1/2 - y, -1/2 + z$; $d = 1 - x, 1 - y, 1 - z$. Selected bond lengths (Å) and angles ($^\circ$): Pb1–O1 = 2.484(2), Pb1–O2 = 2.429(2), Pb1–O3 = 2.418(2), Pb1–O4 = 2.589(2), Pb1–O6 = 2.786(2), Pb1–O7 = 2.912(3), Pb1–O8 = 2.875(3), Pb1–O9 = 2.891(3), P1–O1 = 1.502(3), P2–O2 = 1.504(2), P3–O3 = 1.510(3), P4–O4 = 1.504(3), O1–Pb–O2 = 80.24(8), O1–Pb–O3 = 83.96(8), O1–Pb–O4 = 160.29(9), O2–Pb–O3 = 81.05(9), O2–Pb–O4 = 81.58(8), O3–Pb–O4 = 85.75(8), O6–Pb–O7 = 44.41(10), O8–Pb–O9 = 43.97(8), Pb1–O1–P1 = 144.23(15), Pb1–O2–P2 = 137.26(14), Pb1–O3–P3 = 132.28(15), Pb1–O4–P4 = 131.85(14). (b) The extended structure of $[\text{Pb}(\text{Et}_2(\text{O})\text{P}(\text{CH}_2)_2\text{P}(\text{O})\text{Et}_2)_2(\text{NO}_3)_2]$. Ethyl groups are omitted for clarity.

of the phosphine complex.¹⁸ Interestingly, the *in situ* oxidation of diphosphine ligands has also been reported with Pb(II), when a few crystals of $[\{(\text{Pb}_3(\mu\text{-I})_6)(\text{Ph}_2(\text{O})\text{P}(\text{CH}_2)_2\text{P}(\text{O})\text{Ph}_2)_2\}]\cdot\text{EtOH}$ were obtained from the solvothermal reaction of PbI_2 with KI, I_2 and $\text{Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}_2$. Attempts to increase the yield of the phosphine oxide complex by introducing H_2O_2

into the reaction generated $[\{\text{Pb}_2(\mu\text{-I})_2(\mu^3\text{-I})_2\}\{\text{Ph}_2(\text{O})\text{P}(\text{CH}_2)_2\text{-P}(\text{O})\text{Ph}_2\}]$. Both structures have octahedrally coordinated Pb(II) centres with the $\text{Ph}_2(\text{O})\text{P}(\text{CH}_2)_2\text{P}(\text{O})\text{Ph}_2$ groups bridging between metal centres.¹⁹

Attempts to form diphosphine complexes with $\text{Pb}(\text{BF}_4)_2$ (supplied as a 50% aqueous solution) were largely unsuccessful due to the acidity of the solution (which contains some excess acid to prevent hydrolysis), and led to protonation of the phosphine ligands. This tendency towards ligand protonation has been previously observed when crystals of $[\text{terpyH}_2]\text{-}[\text{BF}_4]_2$ (terpy = 2,2':6',2''-terpyridyl) were obtained from the reaction of aqueous $\text{Pb}(\text{BF}_4)_2$ and terpy.¹² Despite this, on one occasion small colourless crystals of $[\text{Pb}\{\text{Me}_2\text{P}(\text{CH}_2)_2\text{PMe}_2\}\{\text{Me}_2(\text{O})\text{P}(\text{CH}_2)_2\text{P}(\text{O})\text{Me}_2\}][\text{BF}_4]_2\cdot\frac{1}{2}\text{MeNO}_2$ were obtained from the reaction of aqueous $\text{Pb}(\text{BF}_4)_2$ (one mol. equiv.) with two mol. equiv. of $\text{Me}_2\text{P}(\text{CH}_2)_2\text{PMe}_2$ in MeNO_2 . The complex crystallises in the unusual orthorhombic $Fddd$ space group. The preferred coordination mode of both the diphosphine and diphosphine dioxide to lead(II) discussed above is also evident here, as the X-ray structure (Fig. 6a) reveals the $\text{Me}_2\text{P}(\text{CH}_2)_2\text{PMe}_2$ to be symmetrically chelating, while the $\text{Me}_2(\text{O})\text{P}(\text{CH}_2)_2\text{P}(\text{O})\text{Me}_2$ (from the *in situ* oxidation of the diphosphine ligand) bridges between Pb(II) centres, giving an infinite chain structure (Fig. 6b). The symmetry related BF_4^- groups are disordered, but seem to adopt two distinct and reasonably well-defined orientations. Although not discussed in detail because of the disorder, the Pb–F distances in the two orientations are similar at ~ 3.1 and 3.3 Å, allowing the fluoroanion to be described as either κ^1 - or κ^2 -coordinated. Overall the Pb(II) exhibits the expected core (P_2O_2) geometry. There is also a disordered (the N atom is located on a site with 222 symmetry) fractionally occupied (50%) MeNO_2 solvate molecule in the asymmetric unit.

Conclusions

Several new and rare diphosphine complexes of the lead(II) salts $\text{Pb}(\text{NO}_3)_2$ and $\text{Pb}(\text{SiF}_6)$ have been isolated and structurally characterised, revealing a clear preference for a single bidentate phosphine ligand to chelate to lead(II). Unexpectedly, there is no evidence that a second diphosphine can be introduced to the Pb(II) coordination sphere, in marked contrast to the complexes of diimines where bis-ligand complexes predominate.^{11,12} This is unlikely to be due to steric constraints on the large metal centre, and presumably reflects rather limited affinity of the lead(II) for the phosphorus donors. Although the geometries around the Pb(II) are highly irregular, a core four-coordinate motif arranged on one hemisphere of the lead is identifiable in every complex, with longer (weaker) contacts to anions from neighbouring molecules occupying much of the remaining coordination sphere, leading to extended polymer chain and network structures. As with the di- and tri-imine complexes of $\text{Pb}(\text{SiF}_6)$,¹¹ the little studied SiF_6^{2-} dianion can bond to a single Pb(II) ion *via* one or more Pb–F interaction(s), or can bridge between metal centres. The SiF_6^{2-} group is



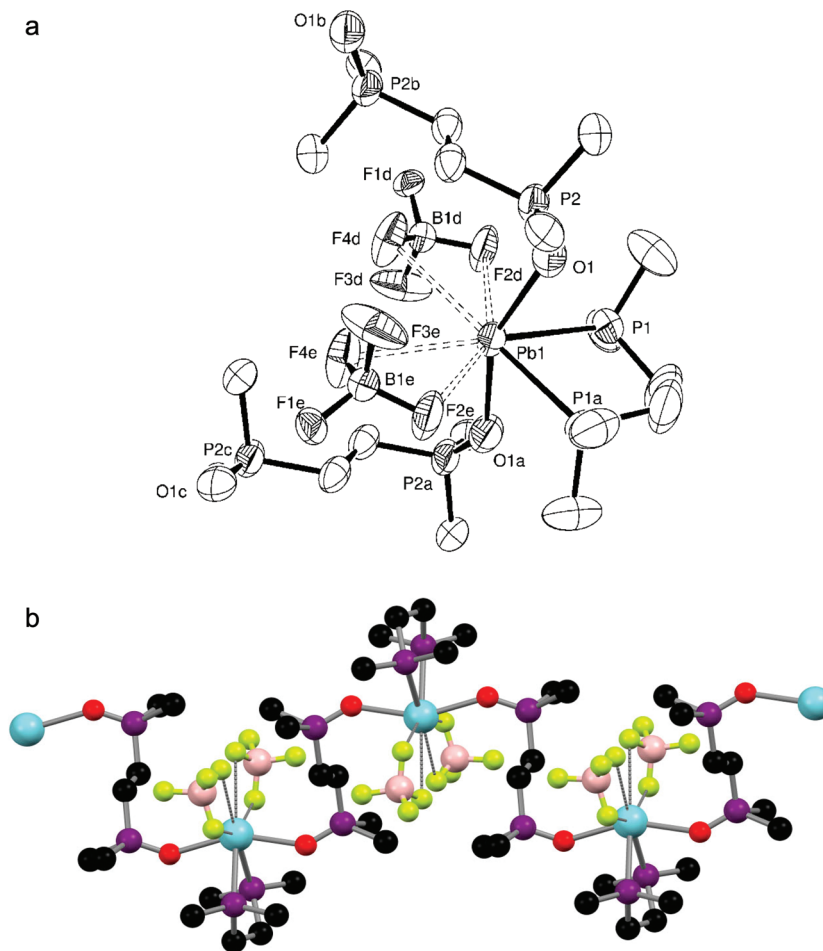


Fig. 6 (a) Structure of $[\text{Pb}(\text{Me}_2\text{P}(\text{CH}_2)_2\text{PMe}_2)\{\text{Me}_2(\text{O})\text{P}(\text{CH}_2)_2\text{P}(\text{O})\text{Me}_2\}][\text{BF}_4]_2 \cdot \frac{1}{2}\text{MeNO}_2$ showing the atom labelling scheme. The displacement ellipsoids are drawn at the 50% probability level and H atoms and the fractionally occupied (50%) MeNO_2 solvate molecule are omitted for clarity. Symmetry operations: $a = 7/4 - x, 3/4 - y, z$; $b = 2 - x, 1 - y, -z$; $c = -1/4 + x, -1/4 + y, -z$; $d = 2 - x, -1/4 + y, -1/4 + z$; $e = -1/4 + x, 1 - y, -1/4 + z$. Selected bond lengths (Å) and angles ($^\circ$): $\text{Pb1}-\text{P1} = 2.789(2)$, $\text{Pb1}-\text{O1} = 2.454(6)$, $\text{O1}-\text{P2} = 1.478(6)$, $\text{P1}-\text{Pb1}-\text{P1a} = 72.86(9)$, $\text{O1}-\text{Pb1}-\text{O1a} = 154.5(3)$, $\text{Pb1}-\text{O1}-\text{P2} = 139.1(3)$. The BF_4 is disordered with two distinct orientations (only one orientation is shown). (b) The extended structure of $[\text{Pb}(\text{Me}_2\text{P}(\text{CH}_2)_2\text{PMe}_2)\{\text{Me}_2(\text{O})\text{P}(\text{CH}_2)_2\text{P}(\text{O})\text{Me}_2\}][\text{BF}_4]_2 \cdot \frac{1}{2}\text{MeNO}_2$. Only one orientation of the BF_4 is shown.

stable in these systems, with no evidence of hydrolysis or fragmentation of the fluoroanion having occurred. This contrasts with the degradation seen for some PF_6^- or BF_4^- salts with $\text{Pb}(\text{II})$ and $\text{Sn}(\text{II})$ macrocyclic species.¹⁰ In some cases adventitious oxygen leads to *in situ* oxidation of diphosphine ligands, yielding the corresponding diphosphine dioxide complexes, where the diphosphine dioxide bridges between lead(II) centres. This remains a challenging area, with poor solubility and the lability of $\text{Pb}(\text{II})$ in solution limiting the information that can be gathered from spectroscopic characterisation.

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