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 Pb(NO₃)₂ with Me₂P-(CH₂)₂PMe₂, α-C₆H₄(PMe₂)₂ or Et₂P(CH₂)₂PMe₂ (L–L) in H₂O/McCN gave white [Pb(L–L)(NO₃)₂], irrespective of the ratio of reagents used. The X-ray structures of [Pb(Me₂P(CH₂)₂PMe₂)(NO₃)₂] and [Pb–(α-C₆H₄(PMe₂)₂)(NO₃)₂] reveal chelating diphosphines and κ²-NO₃ 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 Pb(SiF₆)₂H₂O produced [Pb–(α-C₆H₄(PMe₂)₂)(H₂O)(SiF₆)₂]·H₂O which has a chelating diphosphine, the water molecule and a coordinated SiF₆²⁻ group (which could be described as either κ₁⁺ or asymmetric κ¹⁻-coordinated to the lead), with further Pb–F interactions to neighbouring molecules producing a chain polymer structure. The structure of [Pb(α-C₆H₄(PMe₂)₂)(DMF)₂(SiF₆)]·DMF was also determined and contains dimers with fluorosilicate bridges. Adventitious oxygen readily form diphosphine dioxides complexes, and the structures of [Pb(Et₂O)(CH₂)₂P(O)(Et₂)₃(NO₃)₂] and [Pb(Me₂P(CH₂)₂PMe₂)(Me₂O)(CH₂)₃P(O)(Me₂)]·BF₄ ether produced in this way were determined. The former contains eight-coordinate lead with κ²-NO₃⁻ 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 BF₄⁻ groups completing a very distorted ten-coordinate moiety. Attempts to isolate similar complexes with α-C₆H₄(PPh₂)₂ or α-C₆H₄(AsMe₂)₂ were unsuccessful.

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), and Pb(II)) are well established,⁵ the coordination chemistry has mostly been performed with metal halides,⁵ but includes 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-macroyclic complexes of Pb(NO₃)₂, Pb(BF₄)₂ and Pb(PF₆)₃, 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 Pb(NO₃)₂, or Pb(ClO₄)₂ exhibit high coordination numbers and irregular geometries,¹¹ whilst complexes of these ligands with Pb(BF₄)₂ and Pb(SiF₆)₂ were shown to exhibit a variety of different coordination modes.¹² Here we report the reactions of Pb(NO₃)₂, Pb(SiF₆)₂ and Pb(BF₄)₂ with the diphosphines α-C₆H₄(PMe₂)₂, Me₂P(CH₂)₂PMe₂ and Et₂P(CH₂)₂PMe₂, 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(u) 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(u) nitrate and lead(u) tetrafluoroborate (the latter as 50% solutions in water) were obtained from Aldrich and used as received. Lead(u) hexafluorosilicate dihydrate was obtained from Alfa Aesar and used as received. Lead(II) hexafluorosilicate dihydrate was obtained from Aldrich and used as received. Lead(II) nitrate and lead(II) tetrafluoroborate (the latter as 50% aqueous solution) were obtained from Aldrich and used 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 (λ = 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 focus (S/L) with the crystal held at 100 K (N₂ cryostream). Structure solution and refinements were performed with SHELX-(S/L)9714 focus (S/L) with the crystal held at 100 K (N₂ cryostream).

**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): ν = 1314 (s), 1295 (s), 1033 (s), 837 (sh), 818 (m) (NO₃) cm⁻¹.

**Calc. for C10H16N2O6P2Pb: (529.4) C, 22.7; H, 3.1; N, 5.2.** Found: C, 22.6; H, 3.1; N, 5.2%. IR (Nujol): ν = 1314 (s), 1295 (s), 1033 (s), 446 (s) (SiF₆) cm⁻¹. Small colourless single crystals of the phosphine oxide complex, [Pb(Et₂O)₂][P(CH₃)₂(O)Et₂][NO₃], were grown from layering hexane onto a solution of the isolated powder dissolved in the minimal amount of CH₂Cl₂.

**[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 C₁₄H₁₀O₄P₂O₂Pb: (529.4) C, 22.7; H, 3.1; N, 5.3. Found: C, 22.6; H, 3.1; N, 5.2%. IR (Nujol): ν = 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 C₈H₁₄O₆P₂O₂Pb: (481.4) C, 15.0; H, 3.4; N, 5.8. Found: C, 15.1; H, 3.3; N, 5.8%. IR (Nujol): ν = 1310 (vs, br), 1294 (s), 1033 (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 CH₂CN (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 (CDCl₃, 295 K): δ = 1.19–1.27 (m, [2H₂], CH₃), 1.92–2.02 (m, [4H₄], CH₂), 2.20–2.35 (m, [4H₄], CH₂), 2.40 (d, [4H₄], CH₃). ¹⁳P{¹H} NMR (CD₂Cl₂/CDCl₃, 295 K): δ = 89.3 (s); (223 K): 89.5 (s), Jppb = 2463 Hz); (193 K): 89.6 (s, Jppb = 2532 Hz). IR (Nujol): ν = 1300 (s, br), 1029 (s), 816 (m) (NO₃) cm⁻¹. Small colourless single crystals of the phosphine oxide complex, [Pb(Et₂O)₂][P(CH₃)₂(O)Et₂][NO₃], 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 CH₂CN (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): ν = 3500 (br), 1628 (m, br) (H₂O), 721 (vs, br), 473 (s), 446 (s) (SiF₆) cm⁻¹. 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)₃(P)Me₂}][BF₄]₂[MeNO₂]**

To a degassed solution of Me₂P(CH₂)₃PMe₂ (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 (λ = 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)97 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)₃PMe₂}[NO₃]₂] failed to eliminate the large residual density electron peaks <1 Å.
from Pb1. DFIX restraints were applied to the O–H distances of the lattice H$_2$O in [Pb(o-C$_6$H$_4$(PM$_2$)$_2$)][H$_2$O][SiF$_6$]·H$_2$O. For [Pb(Me$_2$P(CH$_2$)$_2$PMe$_2$)][Me$_2$(O)][P(CH$_2$)$_2$P(O)Me$_2$][BF$_4$]$_2$·2MeNO$_2$, the BF$_4^-$ 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 MeNO$_2$ 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(NO$_3$)$_2$ and Pb(SiF$_6$)$_2$·2H$_2$O, both of which have negligible solubility in organic solvents that are commonly used for phosphine coordination chemistry, such as CH$_3$Cl$_2$ or toluene. Reactions were therefore performed by dissolving Pb(NO$_3$)$_2$ or Pb(SiF$_6$)$_2$·2H$_2$O in the minimum amount of water that had been purged with N$_2$ 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 (CD$_2$Cl$_2$, CD$_3$CN, D$_2$O and CD$_3$OD), 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.

**Lead(II) nitrate complexes**

The reaction of Me$_2$P(CH$_2$)$_2$PMe$_2$ with Pb(NO$_3$)$_2$ in MeCN/H$_2$O formed only the 1:1 [Pb(Me$_2$P(CH$_2$)$_2$PMe$_2$)(NO$_3$)$_2$], 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(Me$_2$P(CH$_2$)$_2$PMe$_2$)(NO$_3$)$_2$] (Fig. 1a) were grown by layering Et$_2$O onto a DMF solution containing the complex. The structure shows the Me$_2$P(CH$_2$)$_2$PMe$_2$ ligand chelated symmetrically to the Pb(II) centre with d(Pb–P) = 2.7918(15) Å while the nitrate groups are asymmetrically k$^2$-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⋯O 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){Pb}₁₂{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 coordinate. 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 diphosphine 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 Cᵥ 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-

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**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. Symmetry operation: a = x, y, −z: 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 = 2.595(5), P1–Pb1–P2 = 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 [Pb(0-C₆H₄(PMe₂)₂](NO₃)₂], which is less clearly resolved for [Pb(Me₂P(CH₂)₂PMe₂](NO₃)₂].

Owing to the unpredictable geometries and the dissociative nature of complexes of Pb(u) in solution, meaningful NMR spectra can generally only be obtained in non-competitive solvents such as CD₂Cl₂, in which both [Pb(Me₂P(CH₂)₂PMe₂](NO₃)₂] and [Pb(0-C₆H₄(PMe₂)₂](NO₃)₂] were found to be insoluble. By using Et₂P(CH₂)₂PET as the ligand with Pb(NO₃)₂ under analogous conditions a white powder, [Et₂P(CH₂)₂PET](NO₃)₂, was isolated which was found to be freely soluble in CD₂Cl₂. There is a significant high frequency shift in the ¹³¹P{¹H} NMR spectrum of this complex confirming that the phosphine is coordinated, while a sharp singlet at δ = 89.3 is observed in the ³¹P{¹H} NMR spectrum. This is a very large, high frequency shift from free' Et₂P(CH₂)₂PET (δ = –18) whose magnitude is mirrored in the shifts seen in Deen et al.⁸ in their in situ NMR studies of phosphine complexes of Pb-(SbF₆)₂. Upon cooling the solution to 223 K, ²⁰⁷Pb satellites were observed, which sharpened upon further cooling to 193 K (¹JPF = 2532 Hz). The appearance of ²⁰⁷Pb satellites only at low temperatures has been reported before in a study of Pb(u) complexes of 2-phosphinobenzenethiolates,¹⁷ and was attributed to ligand lability. Similarly, no resonances were observed in the ²⁰⁷Pb NMR spectrum, even at low temperatures. To ensure that the resonances observed were indeed due to coordinated Et₂P(CH₂)₂PET (i.e. that no unwanted oxidation of the ligand had occurred), an NMR spectrum of the complex was taken in DMSO-d⁶, which displaced the diphosphine and showed the resonance of the uncoordinated Et₂P(CH₂)₂PET. Despite numerous attempts, no crystals of [Pb(Et₂P(CH₂)₂PET)(NO₃)₂] could be grown (instead a few crystals of the phosphine oxide complex [Pb(Et₂O)(P(CH₂)₂P(O)Et₂)(NO₃)₂] were obtained, discussed below); the IR spectrum of [Pb(Et₂P(CH₂)₂PET)(NO₃)₂] indicates that the nitrate groups are again κ²-coordinated (bands at 1300, 1029 and 816 cm⁻¹), which when combined with the NMR spectroscopic evidence suggests that [Pb(Et₂P(CH₂)₂PET)(NO₃)₂] has a similar structure to the other bidentate phosphine complexes.

Although [Pb(Me₂P(CH₂)₂PMe₂](NO₃)₂] and [Pb(0-C₆H₄(PMe₂)₂](NO₃)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 ³¹P{¹H} NMR spectra run in DMF-d⁷, with chemical shifts intermediate between those expected by analogy with the complex [Pb(Et₂P(CH₂)₂PET)(NO₃)₂] and the uncoordinated ligand shifts. The chemical shifts varied widely with concentration, indicating partial disassociation of the diphosphine and rapidly exchanging systems. The values are not quoted. [Pb(Et₂P(CH₂)₂PET)(NO₃)₂] was also found to be partially decomposed by DMF-d⁷.

Under the same reaction conditions the weaker σ-donor and sterically more crowded ligand 0-C₆H₄(PPh₂)₂ did not form a complex with Pb(NO₃)₂. No complex could be isolated with 0-C₆H₄(HasMe₂)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(u) hexafluorosilicate complexes**

The reaction of Pb(SiF₆)·2H₂O with 0-C₆H₄(PMe₂)₂ in a 1 : 1 ratio yielded a white powder which, when dissolved in DMF and layered with Et₂O, gave small colourless crystals of [Pb(0-C₆H₄(PMe₂)₂](H₂O)(SiF₆)]·H₂O. The crystal structure (Fig. 3a) shows the diphosphine to be asymmetrically chelating, with a short Pb–F bond (d(Pb1–F5) = 2.573(3) Å) to a κ²-coordinated SiF₆²⁻ group and a further bond to a water molecule, so that overall the core molecular geometry is very similar to that of [Pb(0-C₆H₄(PMe₂)₂](NO₃)₂] (Fig. 2a), although the disparity in Pb–P bond lengths is greater (~0.03 Å) and the F–Pb–O angle is large (154.76(11)°). 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(Pb1–F1) = 3.201(3), d(Pb1–F4) = 3.167(3) Å) lie well within the sum of the Van der Waal’s radii of 3.49 Å for Pb–F, these long contacts are probably the result of packing within the crystal causing these F atoms to lie close to the Pb(u) centre. Nevertheless, an alternative description for the molecular structure of [Pb(0-C₆H₄(PMe₂)₂](H₂O)(SiF₆)]·H₂O is that the SiF₆²⁻ group is asymmetrically κ²-coordinated. These units are arranged into infinite strands by a Pb–Pb interaction from a neighbouring SiF₆²⁻ group (d(Pb–F) = 2.815(3) Å); two further Pb–Pb interactions with a SiF₆²⁻ group on a parallel strand (d(Pb–F) = 2.795(3), 3.083(3) Å) gives a polymeric chain structure overall (Fig. 3b), where the lead(u) centre is seven coordinate (or nine if the core SiF₆²⁻ group is described as κ³-coordinated). The 0-C₆H₄(PMe₂)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 (HO···OH₂ = 1.89(7) Å), and together these form a hydrogen-bonding network (Fig. 3b) with F atoms on nearby SiF₆²⁻ groups (HO···F = 1.93(2), 2.05(6), 2.14(3) Å).

The IR spectrum of the bulk solid confirms the presence of the SiF₆²⁻ group, although the anion coordination mode cannot be reliably identified.¹⁸ 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.¹¹ Water is also visible in the IR spectrum, indicating that the bulk solid is probably also [Pb(0-C₆H₄(PMe₂)₂](H₂O)(SiF₆)]·xH₂O, though a satisfactory elemental analysis could not be obtained. Poor solubility precluded NMR analysis of this complex.

Repeatition of the reaction with a 2 : 1 (diphosphine : Pb) ratio yielded a few crystals of [Pb(0-C₆H₄(PMe₂)₂](DMF)₂(SiF₆)]·DMF, again demonstrating the preference of the Pb(u) centre to coordinate to just one diphosphine ligand. The asymmetric unit has the expected core bonding environment (P₂F₆O) around the lead, with an O-bonded DMF molecule in place of H₂O, giving a F–Pb–O angle of 140.82(12)°. The SiF₆²⁻ group is now κ²- or κ³-coordinated depending on the viewpoint – the d(Pb1–F3) is ~0.3 Å shorter than the comparable distance in [Pb(0-C₆H₄(PMe₂)₂](H₂O)(SiF₆)]·H₂O, while the d(Pb1–F2)
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 SiF6\(^{2-}\) groups bridging via one F atom per fluoroanion. The orientation of a second DMF molecule close to the Pb(II) centre suggests that is also interacting with the lead (\(d(Pb-O) = 3.263(6)\) Å), which gives an overall coordination number of seven or eight for Pb(II). There is also a DMF solvate molecule in the structure. Formation of this complex also shows that DMF will readily co-ordinate to lead(II), highlighting its unsuitability as a NMR solvent in these systems, but because of the lability of the 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 \([ Pb\{ Et_2P(CH_2)2P(Et_2)\}(NO_3)2]\) by recrystallisation from CH\(_2\)Cl\(_2\) and n-hexane, a few small colourless crystals of \([ Pb\{ Et_2(O)P(CH_2)2P(O)Et_2\}_2(NO_3)2]\) 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 Et\(_2\)(O)P(CH\(_2\))\(_2\)P(O)Et\(_2\) ligands each bridge to different Pb(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)°. Interactions with the nitrate groups are weaker than in \([ Pb\{ L–L\}(NO_3)2]\) (L–L = \(o\)-C\(_6\)H\(_4\)(PMe\(_2\))\(_2\), Me\(_2\)P(CH\(_2\))\(_2\)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 diphenylphosphine 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 Pb\(_4\)P\(_2\)C\(_6\)H\(_4\)P\(_2\) to the crystallographically identified \([ BiCl_3\{ Pb_4P(O)CH_2P(O)Pb_4\}_2]\) having occurred when trying to grow crystals.
of the phosphine complex.\(^{18}\) Interestingly, the \textit{in situ} oxidation of diphosphine ligands has also been reported with Pb(\textit{ii}), when a few crystals of [{\text{Pb}\text{[I]}_2}\text{[Pb} \text{(CH}_2\text{)}_3\text{P(O)}\text{Ph}_2\text{]}_2\text{]}\text{EtOH} were obtained from the solvothermal reaction of PbI\(_2\) with KI, I\(_2\) and Ph\(_2\text{P}(\text{CH}_2\text{)}_2\text{PPh}_2\). Attempts to increase the yield of the phosphine oxide complex by introducing H\(_2\text{O}_2\) into the reaction generated [{\text{Pb}\text{[I]}_2}\text{[Pb} \text{(CH}_2\text{)}_3\text{P(O)}\text{Ph}_2\text{]}_2\text{]}\text{EtOH}]. Both structures have octahedrally coordinated Pb(\textit{ii}) centres with the Pb\(_2\text{(O)}\text{(CH}_2\text{)}_3\text{P(O)}\text{Ph}_2\) groups bridging between metal centres.\(^ {19}\)

Attempts to form diphosphine complexes with Pb(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{[BF}_4\text{]}_2\text{]} (terpy = \text{2,2′,6′,2′-terpyridyl}) were obtained from the reaction of aqueous Pb(BF\(_4\))\(_2\) and terpy.\(^ {12}\) Despite this, on one occasion small colourless crystals of [{\text{Me}_2\text{P(} \text{CH}_2\text{)}_3\text{PMe}_2}\text{]}\text{BF}_4\]\text{[BF}_4\text{]}_2\text{MeNO}_2 were obtained from the reaction of aqueous Pb(BF\(_4\))\(_2\) (one mol. equiv.) with two mol. equiv. of Me\(_2\text{P(} \text{CH}_2\text{)}_3\text{PMe}_2\) in MeNO\(_2\). The complexes crystallised in the unusual orthorhombic \(\text{Fd} \text{dd}\) space group. The preferred coordination mode of both the diphosphine and diphosphine dioxide to lead(\textit{ii}) discussed above is also evident here, as the X-ray structure (Fig. 6a) reveals the Me\(_2\text{P(} \text{CH}_2\text{)}_3\text{PMe}_2\) to be symmetrically chelating, while the Me\(_2\text{O}\text{[P(} \text{CH}_2\text{)}_3\text{P(O)Me}_2\)]\text{BF}_4\]\text{[BF}_4\text{]}_2\text{MeNO}_2 exhibits the expected core (P\(_2\)O\(_2\)) 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.

![Diagram](image.png)

**Fig. 5** (a) Crystal structure of [{\text{Pb}\text{[Et}_2\text{(O)P(} \text{CH}_2\text{)}_2\text{P(O)Et}_2\text{]}_2\text{(NO}_3\text{)}_2\text{]} 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 (°): Pb\(_1\)–O\(_1\) = 2.484(2), Pb\(_1\)–O\(_2\) = 2.429(2), Pb\(_1\)–O\(_3\) = 2.418(2), Pb\(_1\)–O\(_4\) = 2.589(2), Pb\(_1\)–O\(_6\) = 2.786(2), Pb\(_1\)–O\(_7\) = 2.912(3), Pb\(_1\)–O\(_8\) = 2.875(3), Pb\(_1\)–O\(_9\) = 2.891(3), P\(_1\)–P\(_2\) = 1.502(3), P\(_1\)–P\(_2\) = 1.504(2), P\(_3\)–O\(_3\) = 1.510(3), P\(_4\)–O\(_4\) = 1.504(3), O\(_1\)–Pb\(_1\)–O\(_2\) = 80.24(8), O\(_1\)–Pb\(_1\)–O\(_3\) = 83.96(8), O\(_1\)–Pb\(_1\)–O\(_4\) = 160.29(9), O\(_2\)–Pb\(_1\)–O\(_3\) = 81.05(9), O\(_2\)–Pb\(_1\)–O\(_4\) = 81.58(8), O\(_3\)–Pb\(_1\)–O\(_4\) = 85.75(8), O\(_6\)–Pb\(_1\)–O\(_7\) = 44.41(10), O\(_8\)–Pb\(_1\)–O\(_9\) = 43.97(8), Pb\(_1\)–O\(_1\)–P\(_1\) = 144.23(15), Pb\(_1\)–O\(_2\)–P\(_2\) = 137.26(14), Pb\(_1\)–O\(_3\)–P\(_3\) = 132.28(15), Pb\(_1\)–O\(_4\)–P\(_4\) = 131.85(14). (b) The extended structure of [{\text{Pb}\text{[Et}_2\text{(O)P(} \text{CH}_2\text{)}_2\text{P(O)Et}_2\text{]}_2\text{(NO}_3\text{)}_2\text{]}\text{EtOH}. Ethyl groups are omitted for clarity.

**Conclusions**

Several new and rare diphosphine complexes of the lead(\textit{ii}) salts Pb(NO\(_3\))\(_2\) and Pb(SiF\(_6\))\(_2\) have been isolated and structurally characterised, revealing a clear preference for a single bidentate phosphine ligand to chelate to lead(\textit{ii}). Unexpectedly, there is no evidence that a second diphosphine can be introduced to the Pb(\textit{ii}) coordination sphere, in marked contrast to the complexes of diimine ligands discussed above. This is unlikely to be due to steric constraints on the large metal centre, and presumably reflects rather limited affinity of the lead(\textit{ii}) for the phosphorus donors. Although the geometries around the Pb(\textit{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 Pb(SiF\(_6\))\(_2\), the little studied SiF\(_6\)\(^{2–}\) dianion can bond to a single Pb(\textit{ii}) ion via one or more Pb–F interaction(s), or can bridge between metal centres. The SiF\(_6\)\(^{2–}\) group is...
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 Pb(II) and Sn(II) macrocyclic species.\textsuperscript{10} In some cases adventitious oxygen leads to \textit{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 Pb(II) in solution limiting the information that can be gathered from spectroscopic characterisation.

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