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Hexafluorosilicate and tetrafluoroborate coordination to lead(II) di- and tri-imine complexes – Unusual fluoroanion coordination modes

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ABSTRACT

Lead(II) tetrafluoroborate and hexafluorosilicate complexes with 2,2′-bipyridyl, 1,10-phenathroline and 2,2′:6′,2″-terpyridyl have been prepared from the ligand and lead salt in aqueous/MeCN. Crystal structures are reported for $[Pb(bipy)_2(SiF_6)]$, $[Pb(phen)_2(SiF_6)]$ and $[Pb(bipy)_2(BF_4)_2]$ which are dinuclear with each lead coordinated "*cis*" to the two diimines and with the bridging fluoroanions completing eight or nine-coordination. $[Pb(phen)_2(BF_4)_2]$ is eight-coordinate and mononuclear with "*cis*" diimines and two κ^2-BF_4^- groups. $[Pb(phen)_2(H_2O)_2(SiF_6)]$ is also mononuclear with a κ^2-SiF_6^{2-} group and two coordinated water molecules. Reaction of $Pb(BF_4)_2$ with 2,2′:6′,2″-terpyridyl gave only $[Pb(terpy)_3][BF_4]_2$, but $Pb(SiF_6)$ produced $[Pb(terpy)(H_2O)(SiF_6)]$, which is a chain polymer with bridging SiF_6^{2-} groups and significant π-stacking of the imine rings. The work has identified a number of coordination modes of the SiF_6^{2-} anion, which has been little used in coordination chemistry but proves to be versatile and also stable (to decomposition/hydrolysis).

1. Introduction

'Non-coordinating' anions have played a key role in many areas of coordination and organometallic chemistry and catalysis, despite the recognition that in appropriate cases anion coordination does occur, and sometimes this can be surprisingly strong [1–4]. More recently, efforts have focussed on designing anions with a weaker coordinating ability than the archetypal examples ClO_4^- or $CF_3SO_3^-$, such as fluorinated-arylborates or -aluminates [4]. With the majority of metal ions fluoroanions such as BF_4^-, PF_6^- or SbF_6^- have a very limited tendency to coordinate. They are also usually chemically inert and are much more readily available than fluorinated-arylborates or -aluminates. In a recent investigation of lead(II) complexes with crown ethers, oxathia- and oxaselena-macrocycles, we used lead(II) tetrafluoroborate or hexafluorophosphate as sources of lead(II), and found that not only did the fluoroanions readily enter the first coordination sphere of the lead to exhibit a range of coordination modes (κ^1, κ^2, or μ^2), but also that they were readily decomposed in some systems, with formation of coordinated or free fluoride [5]. Decomposition of the anions also occurred in some tin(II) crown ether systems [6]. In order to explore both the coordinating abilities of fluoroanions and this unexpected reactivity, we investigated lead(II) tetrafluoroborate and hexafluorosilicate complexes of 2,2′-bipyridyl (bipy), 1,10-phenanthroline (phen) and 2,2′:6′,2″-terpyridyl (terpy), and report the results here. A large number of lead(II) complexes with these imine ligands are known, but most are with oxoanions (ClO_4^-, NO_3^- or O_2CR^-, *etc.*) [7]. The $[Pb(bipy)_x(PF_6)_2]$ ($x = 2$ or 4) have recently been described [8], hence we did not include the hexafluorophosphate complexes in this work. Lead, with a covalent radius of 1.46 Å, often forms compounds with high coordination numbers and with irregular geometries, which reflect both the steric demands of the ligands and inter-ligand replusions. The presence of a formal lone pair, which may or may not be stereochemically active, may also influence the geometries observed [7].

2. Results and discussion

The lead(II) salts used for the syntheses were an aqueous solution of $Pb(BF_4)_2$, and solid $Pb(SiF_6)\cdot 2H_2O$, which was dissolved in the minimum volume of water. The structure of the latter contains nine-coordinate lead in two environments, one provided by six fluorides and three water molecules, the other with five fluorines and four water molecules [9]. The $Pb(BF_4)_2$ solution, as supplied, contains some excess acid to prevent hydrolysis. The acid caused no problems with bipy or phen, but crystals obtained from the terpy reaction were reproducibly found by X-ray crystal structure determination to be $[terpyH_2][BF_4]_2$. The excess acid could be removed by stirring the solution with lead carbonate for a few minutes, after

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which it was filtered and the filtrate used immediately. Reaction of this with terpy yielded $[Pb(terpy)_3][BF_4]_2$. The reaction of $Pb(BF_4)_2$ or $Pb(SiF_6)$ with either bipy or phen (or terpy, in the case of $Pb(SiF_6)$) in a mixture of H_2O and MeCN, afforded white, beige or pale pink solids. Crystals were obtained by allowing aliquots of the reaction solutions to evaporate slowly in air. Although water is not evident in the IR spectra of the bulk powders, (after washing with diethyl ether and drying *in vacuo*), water is present in several of the crystal structures.

2.1. X-ray structures

As a result of the labile nature of Pb(II) in solution and the unpredictable geometries present, the information provided by spectroscopic techniques is quite limited. X-ray crystallographic analysis is the key characterisation technique for complexes of this type and therefore the structural features of the new complexes are described first, followed by a discussion of relevant spectroscopic data. Microanalytical data confirm the stoichiometries of the bulk samples.

The structure of $[Pb(bipy)_2(SiF_6)]$ (Fig. 1) shows it to be a centrosymmetric dimer. Each lead ion is coordinated to two chelating bipy ligands, disposed "*cis*" with d(Pb–N) = 2.531(5)–2.760(5) Å. These values can be compared with those reported for $[Pb(bipy)_2(Y)_2]$ (Y = ClO_4, NO_3), which are also dimers with bridging oxo-anions [10], with d(Pb–N) in the range 2.512(7)–2.646(8) Å. The inter-ligand ∠N–Pb–N angles are also quite similar in the three structures. The coordination of the bridging SiF_6^{2-} groups shows four of the fluorines interacting with the lead centres, three (F4, F5 and F6) coordinate to a single lead centre (Pb–F = 2.750(2), 2.811(2), 2.722(4) Å), whilst F1 bridges the two leads in an unsymmetrical manner with longer bonds (Pb1–F1 = 2.974(2), Pb1–F1a = 2.911(2) Å). For comparison, the sum of the van der Waals radii for Pb and F is 3.49 Å [11], and all the Pb–F distances are well within this. Overall, the lead is in a distorted nine-coordinate environment (N_4F_5). The $[Pb(bipy)_2(Y)_2]$ (Y = ClO_4, NO_3) [10] have similar geometries (N_4O_5), suggesting this arrangement maximises the lead-donor group interactions, irrespective of whether the anions present are planar, tetrahedral or octahedral.

The bulk product isolated from the reaction of $Pb(SiF_6)$ and phen was the analogous $[Pb(phen)_2(SiF_6)]$, but the crystals grown from the solution were found to have the structure $[\{Pb(phen)_2(SiF_6)\}_2]\cdot[Pb(phen)_2(H_2O)_2(SiF_6)]\cdot 11H_2O$, containing two lead complexes; the dimeric $[\{Pb(phen)_2(SiF_6)\}_2]$ and a monomer with two coordinated water molecules, $[Pb(phen)_2(H_2O)_2(SiF_6)]$. The former has the structure shown in Fig. 2, and is quite similar to that of the bipy complex discussed above, although the phen complex is not centrosymmetric. Nonetheless, it also has nine-coordinate lead(II) with similar coordination of the SiF_6^{2-} units. The monomeric $[Pb(phen)_2(Y)_2]$ (Y = ClO_4, NO_3) [12] have a similar PbN_4 unit and achieve eight-coordination overall when the Pb–O bonds are considered.

The structure of $[Pb(phen)_2(H_2O)_2(SiF_6)]$ (Fig. 3) reveals a discrete monomer with eight-coordinate lead, through two chelating phen molecules "*cis*" disposed, an asymmetrically chelating (κ^2) SiF_6^{2-} group (Pb–F = 3.272(5), 2.701(5) Å), and two water molecules. Unusually, the crystal $[\{Pb(phen)_2(SiF_6)\}_2]\cdot[Pb(phen)_2(H_2O)_2(SiF_6)]\cdot 11H_2O$ also contains eleven lattice water molecules, although the hydrogen-bonding expected for the latter could not be satisfactorily modelled and may vary within the crystal.

The crystal structure of $[Pb(bipy)_2(BF_4)_2]$ revealed it to be a dimer, with a fractionally occupied (50%) water molecule sitting between the lead centres, i.e. $[\{Pb(bipy)_2(BF_4)_2(H_2O)_{0.25}\}_2]$ (Fig. 4). The structure is surprisingly complicated; the PbN_4 geometry is similar to that found in the other diimine complexes [10,12], but instead of there being four μ^2-BF_4^- groups as one might have expected, the coordination sphere of each lead centre is completed by four fluorines from three BF_4^- anions, one of which is κ^1, one is κ^2, one is μ^2, and the fourth one chelates (κ^2) to one lead and forms a single bridge to the second lead. This gives eight- (or nine- when the water is present) coordinate lead centres. The Pb–F distances span the range 2.725(8)–3.028(9) Å, and probably reflect the packing within the crystal lattice rather than any strong directional preference.

In contrast, $[Pb(phen)_2(BF_4)_2]$ is monomeric, with eight-coordinate lead, composed of two chelating diimines and two κ^2-BF_4^- groups (Fig. 5), and thus is closely related to that of $[Pb(phen)_2(H_2O)_2(SiF_6)]$, with the two water molecules replaced by a chelating tetrafluoroborate anion. The Pb–F bonds are surprisingly disparate (by ~0.15 Å) between the two anions.

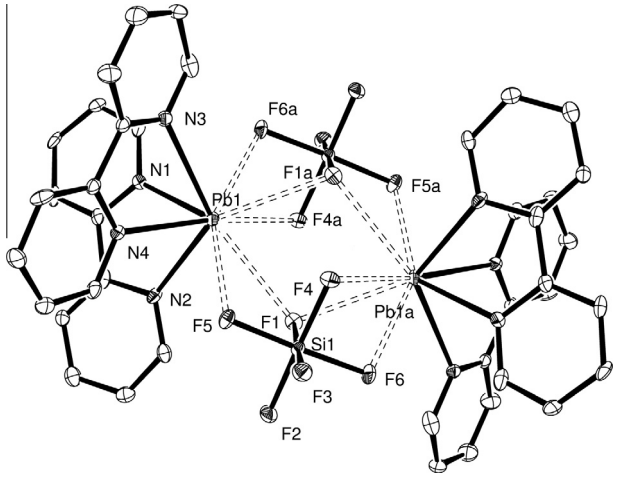

Fig. 1. Structure of the SiF_6-bridged dimer present in $[Pb(bipy)_2(SiF_6)]$ showing the atom labelling scheme. The displacement ellipsoids are drawn at the 50% probability level and H atoms are omitted for clarity. Symmetry operation: a = 2 – *x*, –*y*, 1 – *z*. Selected bond lengths (Å) and angles (°): Pb1–N1 = 2.531(5), Pb1–N2 = 2.553(5), Pb1–N3 = 2.760(5), Pb1–N4 = 2.643(5), Pb1–F1 = 2.974(2), Pb1–F5 = 2.750(2), Pb1–F1a = 2.911(2), Pb1–F4a = 2.811(2), Pb1–F6a = 2.722(4), N1–Pb1–N2 = 64.01(16), N3–Pb1–N4 = 60.61(16).

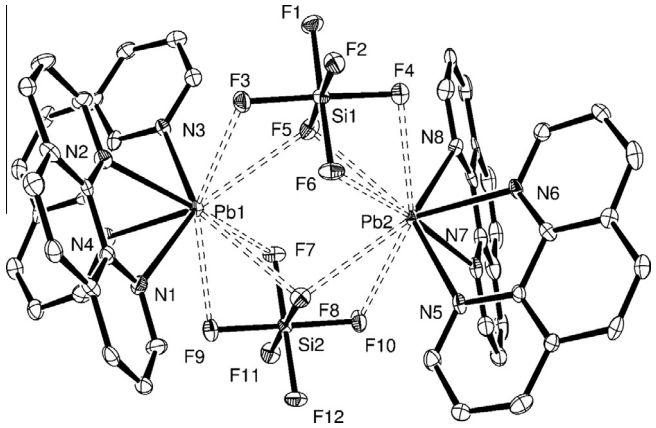

Fig. 2. Structure of the dimeric unit present in $[Pb(phen)_2(SiF_6)]$ showing the atom labelling scheme. The displacement ellipsoids are drawn at the 50% probability level and H atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Pb1–N1 = 2.667(5), Pb1–N2 = 2.603(5), Pb1–N3 = 2.591(5), Pb1–N4 = 2.509(5), Pb2–N5 = 2.536(5), Pb2–N6 = 2.522(5), Pb2–N7 = 2.542(5), Pb2–N8 = 2.627(5), Pb1–F3 = 2.724(3), Pb1–F5 = 3.072(5), Pb1–F7 = 2.791(4), Pb1–F8 = 2.948(4), Pb1–F9 = 2.836(5), Pb2–F4 = 2.894(4), Pb2–F5 = 2.951(4), Pb2–F6 = 2.875(4), Pb2–F8 = 3.060(5), Pb2–F10 = 2.817(4), N1–Pb1–N2 = 62.77(14), N3–Pb1–N4 = 65.27(15), N5–Pb2–N6 = 65.59(15), N7–Pb2–N8 = 64.37(16).

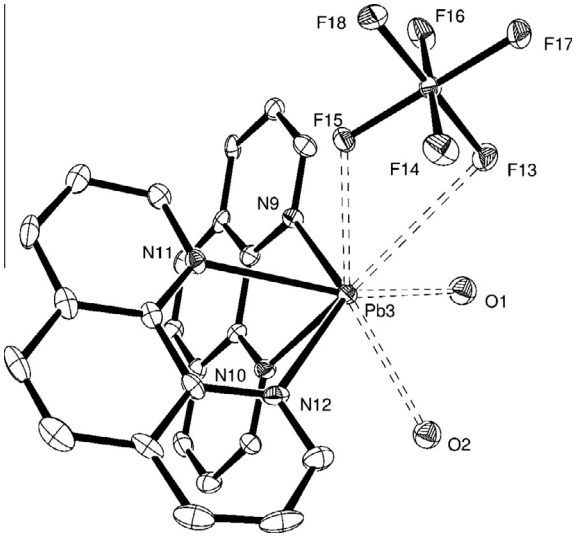

Fig. 3. Structure of $[Pb(phen)_2(H_2O)_2(SiF_6)]$ showing the atom labelling scheme. The displacement ellipsoids are drawn at the 50% probability level and H atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Pb3–N9 = 2.561(5), Pb3–N10 = 2.513(5), Pb3–N11 = 2.677(5), Pb3–N12 = 2.654(5), Pb3–O1 = 2.778(5), Pb3–O2 = 2.800(3), Pb3–F13 = 3.272(5), Pb3–F15 = 2.701(5), N9–Pb3–N10 = 65.44(15), N11–Pb3–N12 = 61.95(14).

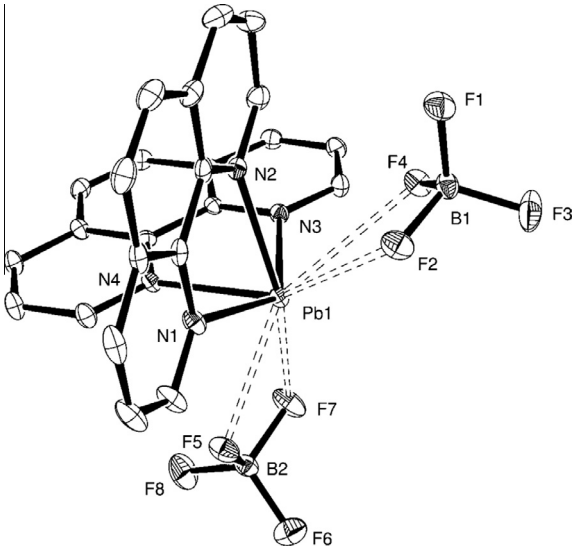

Fig. 5. Structure of $[Pb(phen)_2(BF_4)_2]$ showing the atom labelling scheme. The displacement ellipsoids are drawn at the 50% probability level and H atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Pb1–N1 = 2.539(2), Pb1–N2 = 2.483(2), Pb1–N3 = 2.549(2), Pb1–N4 = 2.445(2), Pb1–F2 = 3.038(17), Pb1–F4 = 3.010(14), Pb1–F5 = 2.751(11), Pb1–F7 = 2.845(15), N1–Pb1–N2 = 66.40(7), N3–Pb1–N4 = 66.62(6).

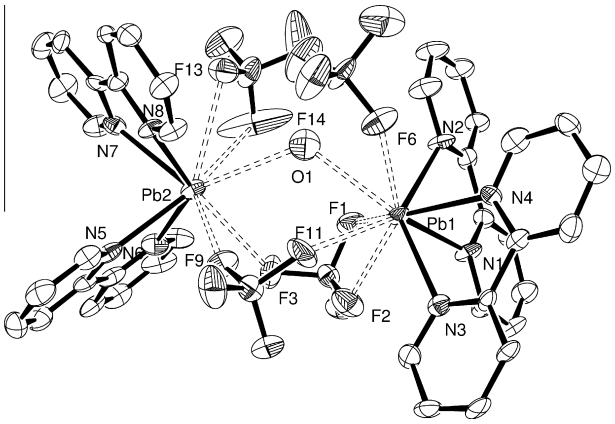

Fig. 4. Structure of $[\{Pb(bipy)_2(BF_4)_2(H_2O)_{0.25}\}_2]$ showing the atom labelling scheme. The displacement ellipsoids are drawn at the 50% probability level and H atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Pb1–N1 = 2.516(8), Pb1–N2 = 2.503(8), Pb1–N3 = 2.558(8), Pb1–N4 = 2.514(9), Pb1–O1 = 2.836(8), Pb1–F1 = 3.017(10), Pb1–F2 = 2.802(9), Pb1–F6 = 2.767(10), Pb1–F11 = 3.007(8), Pb2–N5 = 2.533(9), Pb2–N6 = 2.509(9), Pb2–N7 = 2.541(9), Pb2–N8 = 2.486(8), Pb2–O1 = 2.916(8), Pb2–F3 = 2.958(8), Pb2–F9 = 2.725(8), Pb2–F13 = 2.946(11), Pb2–F14 = 3.028(9), N1–Pb1–N2 = 64.8(3), N3–Pb1–N4 = 64.7(3), N5–Pb2–N6 = 64.5(3), N7–Pb2–N8 = 65.1(3).

The literature structure [8] of the dimeric $[Pb(bipy)_2(PF_6)_2]$ also shows Pb–F contacts significantly within the van der Waals radii sum, and reveals the complexity of fluoroanion coordination in these systems. Although not discussed by the authors, the structure (Fig. 6) shows each lead is κ^2-coordinated to a PF_6^- group, whilst a third PF_6^- group is coordinated in an asymmetric κ^3 mode, and the fourth PF_6^- κ^2-coordinated to one lead and bridging to the second one *via* a long Pb–F interaction.

In summary, the core geometry of the $Pb(diimine)_2$ units has the diimines "*cis*" disposed on one hemisphere of the lead, and is relatively little affected by the anions present, which tend to fill the remaining space around the lead centre. In contrast to oxo-anions, which coordinate strongly to the lead [7,8,10,12], the coordination adopted with the weakly bound fluoroanions is likely to be influenced by crystal packing effects, which results in the irregular and varying geometries found.

Different structures are found in the complexes of terpy. Species with a 1:1 Pb:terpy ratio were reported with lead(II) halides or oxo-salts [13], which have 1-D chain structures and bridging anions. The fluorosilicate complex prepared in this work has the formula $[Pb(terpy)(H_2O)(SiF_6)]$ and shows a planar N_3-coordinated terpy. The coordinated water is disordered above and below the PbN_3 plane. The Pb–O distances (2.87(2) and 3.05(1) Å) are very long (although still well within the sum of the van der Waals radii, 3.5 Å), suggesting weak interactions. Both the microanalysis and the IR spectrum indicate the bulk sample is anhydrous; the coordinated water present in the crystal structure presumably fills a void in the lattice, and is easily removed *in vacuo*. The SiF_6^{2-} groups linking the lead-terpy units into chains are disordered (Fig. 7), but seem to adopt two distinct and reasonably well-defined orientations. The Si–F distances are not significantly different to those found in the free anion (~1.70 Å) [14], but the Pb–F bond distances span a wide range and, in view of the disorder, are not discussed here (although they are included in the CIF). The coordinated F1A/F1B site positions refine very close together and strongly suggest this atom position is identical for both orientations. Although one must interpret the dimensions with care because of this disorder, it appears that in one orientation, the SiF_6^{2-} units bridge the lead centres ($\kappa^2\kappa'^2$) using a planar SiF_4 group (with no interaction with the remaining *trans* F–Si–F unit). The second orientation has the SiF_6^{2-} units bridging the lead centres ($\kappa^3\kappa'^3$), although within each set of three (*fac*) fluorides there are three disparate Pb–F bond lengths (~2.49 to ~3.22 Å). The terpy groups also show π-stacking between neighboring chains (Fig. 7), with the distance between the planes = 3.566 Å.

As mentioned above, reaction of terpy with $Pb(BF_4)_2$ gave $[Pb(terpy)_3][BF_4]_2$. The cation has been reported before in the ClO_4^- salt [13], in which the cation is disordered. The structure of $[Pb(terpy)_3][BF_4]_2$ is described in ESI, and although this is also disordered, the disorder has been successfully modelled in the alternative space-group P–3c1, which avoids the unreasonably close approach of some atoms in the reported structure [15].

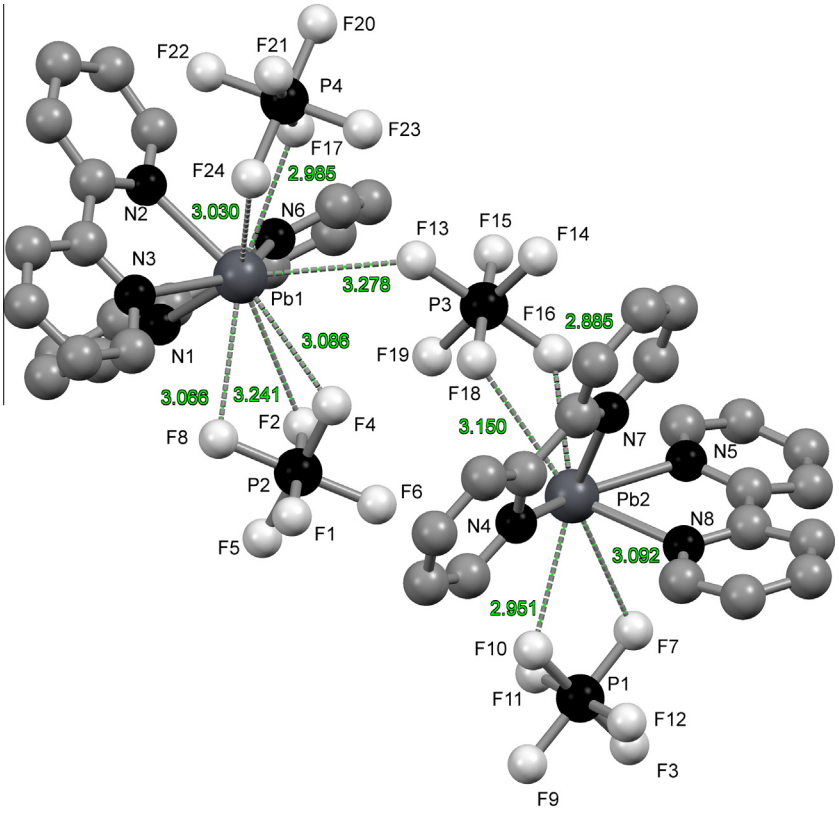

Fig. 6. View showing the fluoroanion coordination in $[Pb(bipy)_2(PF_6)_2]$ redrawn from the data in Ref. [8].

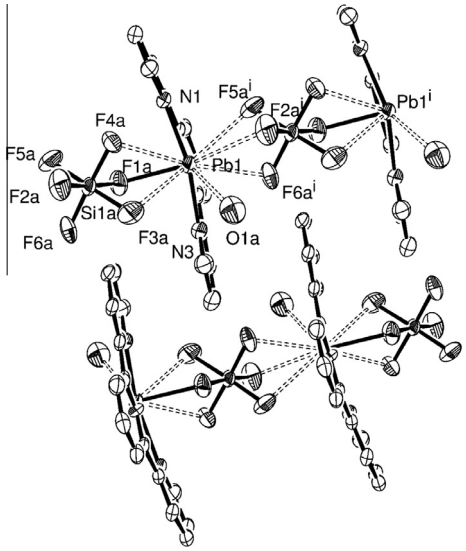

Fig. 7. Crystal structure of $[Pb(terpy)(H_2O)(SiF_6)]$ showing the atom labelling scheme. The displacement ellipsoids are drawn at the 50% probability level and H atoms are omitted for clarity. Selected bond lengths (Å): Pb1–N1 = 2.550(6), Pb1–N2 = 2.491(6), Pb1–N3 = 2.480(7), Pb1–O1A = 2.87(2). The SiF_6 is rotationally disordered roughly about the F1–Si–F2 axis, (only one orientation is shown). This was refined in two parts and the occupancies converged at *ca.* 50/50. The distance between the planes of the stacking terpy rings is 3.566 Å.

The coordination modes of the BF_4^- and PF_6^- groups to Pb(II) described above are similar to those observed in other systems, including the crown ether, thia- and selena-crown systems [5], and demonstrate that F···Pb coordination is favoured. The unusual dimer structure of $[Pb(bipy)_2(BF_4)_2]$, which shows four different coordination modes of the BF_4^- groups, probably indicates there is little to choose between them on bond energy grounds, and the structure adopted reflects crystal packing requirements, maximising the lattice energy.

These are the first examples of SiF_6^{2-} coordinated to lead. The CSD [16] shows that whilst numerous examples of SiF_6^{2-} coordinated *via* two *trans* fluorines to zinc(II) in pillared coordination networks are known [17], other coordination modes are very rare. Chelation (κ^2-coordination) to Cu(II) occurs in $[CuL(SiF_6)]$ (L = pyridyl-pyrazol ligand) [18], or to Zn(II) in $[Zn(phen)_2(SiF_6)]$ [19]. The present work has revealed examples of SiF_6^{2-} κ^2-coordinated to a single lead(II) in $[Pb(phen)_2(H_2O)_2(SiF_6)]$, whilst in the dinuclear complexes ($[Pb(bipy)_2(SiF_6)]$ and $[Pb(phen)_2(SiF_6)]$) four of the fluorines from each SiF_6^{2-} interact with the lead centres: three fluorines coordinate to a single lead centre, while the fourth bridges the two lead centres in an unsymmetrical manner. Description of the coordination in $[Pb(terpy)(H_2O)(SiF_6)]$ is complicated by the disorder present, but, depending on the coordination of the SiF_6^{2-} unit, the lead is either 8- or 10-coordinate (the latter is shown in Fig. 7); the π-stacking between neighbouring chains also plays a role here.

2.2. Spectroscopic data

The detailed information that can be obtained from spectroscopic data on this series of Pb(II) complexes is limited. The IR spectra (Nujol) do confirm the presence of the imines and the fluoroanions (Experimental), but do not reliably distinguish the anion coordination modes. The stretching modes of the BF_4^- and SiF_6^{2-} groups are significantly broadened, although resolved splittings which might be expected in view of the lower symmetries arising from the Pb(II) coordination are not seen, presumably because these interactions are weak. The ^1H NMR spectra (CD_3CN or D_2O

solution) show the imine resonances shifted to high frequency, consistent with coordination, but the $^{19}F\{^1H\}$ NMR spectra show resonances consistent with 'free' fluoroanions, indicating that the coordination observed in the solid state does not persist to any significant extent in solution; the anions are probably displaced by the NMR solvent (the complexes are poorly soluble in weakly coordinating solvents such as CH_2Cl_2). Notably, and in contrast to the results in the Pb(II) crown ether systems [5], there was no evidence for decomposition of the fluoroanions in any of the new complexes reported here.

3. Experimental

The ligands and lead tetrafluoroborate (50% solution in water) were obtained from Aldrich, and lead hexafluorosilicate dihydrate from Alfa Aesar, and were used as received. 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 $^{19}F\{^1H\}$ NMR spectra were recorded using a Bruker DPX-400 spectrometer and referenced to the residual solvent resonance and external $CFCl_3$ respectively. Microanalytical measurements were performed by London Metropolitan University.

3.1. [Pb(bipy)$_2$(BF$_4$)$_2$]

$Pb(BF_4)_2$ as a 50% aqueous solution (0.206 g, 0.27 mmol) was added to a solution of 2,2′-bipyridyl (0.081 g, 0.52 mmol) in CH_3CN (5 mL), leading to the precipitation of a small amount of fine white powder. The reaction mixture was stirred for 24 h, then it was filtered and a portion was removed for crystal growth. From the remaining solution, the solvent was removed *in vacuo* to yield a pale pink powder, which was washed with Et_2O (5 mL) and dried *in vacuo*. Yield: 0.113 g, 60%. *Anal.* Calc. for $C_{20}H_{16}B_2F_8N_4Pb$: C, 34.7; H, 2.3; N, 8.1. Found: C, 34.7; H, 2.4; N, 8.2%. ^1H NMR (CD_3CN, 295 K): δ = 7.78 (ddd, [2H]), 8.29 (td, [2H]), 8.42 (d, [2H]), 8.74 (dd, [2H]). $^{19}F\{^1H\}$ NMR (CD_3CN, 295 K): δ = −150.6 (s). IR (Nujol): ν = 1066 (vs, br), 520 (m) (BF_4) cm^{-1}. Slow evaporation of a portion of the reaction mixture yielded colourless crystals of $[\{Pb(bipy)_2(BF_4)_2(H_2O)_{0.25}\}_2]$.

3.2. [Pb(bipy)$_2$(SiF$_6$)]

A solution of 2,2′-bipyridyl (0.081 g, 0.52 mmol) in CH_3CN (5 mL) was added to $Pb(SiF_6)\cdot 2H_2O$ (0.100 g, 0.26 mmol) dissolved in deionised water (15 mL), leading to the precipitation of a small amount of fine white powder. The reaction mixture was stirred for 1 h, then it was filtered and a small aliquot removed for crystal growth. The solvent was removed *in vacuo* from the rest, to yield a pale pink powder, which was washed with Et_2O (5 mL) and dried *in vacuo*. Yield: 0.062 g, 36%. *Anal.* Calc. for $C_{20}H_{16}F_6N_4PbSi$: C, 36.3; H, 2.4; N, 8.5. Found: C, 36.7; H, 2.5; N, 8.5%. ^1H NMR (D_2O, 295 K): δ = 7.57 (br s, [2H]), 8.03 (br s, [2H]), 8.09 (t, [2H]), 8.61 (br s, [2H]). $^{19}F\{^1H\}$ NMR (D_2O, 295 K): δ = −130.1 (s, $^1J_{SiF}$ = 109 Hz). IR (Nujol): ν = 755 (vs, br), 482 (m), 474 (s), 460 (m) (SiF_6) cm^{-1}. Slow evaporation of a portion of the reaction mixture yielded colourless crystals of $[Pb(bipy)_2(SiF_6)]$.

3.3. [Pb(phen)$_2$(BF$_4$)$_2$]

$Pb(BF_4)_2$ as a 50% aqueous solution (0.197 g, 0.26 mmol) was added to a solution of 1,10-phenanthroline (0.095 g, 0.52 mmol) in CH_3CN (5 mL), leading to the precipitation of a small amount of fine white powder. The reaction mixture was stirred for 2 h, then it was filtered and the solvent removed *in vacuo* to yield a white powder, which was washed with Et_2O (5 mL) and dried *in vacuo*. Yield: 0.107 g, 56%. *Anal.* Calc. for $C_{24}H_{16}B_2F_8N_4Pb$: C, 38.9; H, 2.2; N, 7.6. Found: C, 38.7; H, 2.1; N, 7.4%. ^1H NMR (CD_3CN, 295 K): δ = 8.03 (br s, [2H]), 8.12 (br s, [2H]), 8.75 (s, [2H]), 9.11 (br s, [2H]). $^{19}F\{^1H\}$ NMR (CD_3CN, 295 K): δ = −150.4 (s). IR (Nujol): ν = 1058 (vs, br), 523 (s) (BF_4) cm^{-1}. Slow evaporation of a portion of the reaction mixture yielded colourless crystals of $[Pb(phen)_2(BF_4)_2]$.

3.4. [Pb(phen)$_2$(SiF$_6$)]

A solution of 1,10-phenanthroline (0.100 g, 0.55 mmol) in CH_3CN (5 mL) was added to $Pb(SiF_6)\cdot 2H_2O$ (0.102 g, 0.26 mmol) dissolved in deionised water (15 mL), giving a colourless solution. The reaction mixture was stirred for 2 h, then the solvent volume was reduced *in vacuo* until a white powder precipitated, which was isolated by filtration, washed with CH_3CN and dried *in vacuo*. Yield: 0.045 g, 23%. *Anal.* Calc. for $C_{24}H_{16}F_6N_4PbSi$: C, 40.6; H, 2.3; N, 7.9. Found: C, 40.5; H, 2.2; N, 7.5%. ^1H NMR (D_2O, 295 K): δ = 7.93 (dd, [2H]), 7.97 (s, [2H]), 8.62 (dd, [2H]), 9.03 (dd, [2H]). $^{19}F\{^1H\}$ NMR (D_2O, 295 K): δ = −129.7 (s, $^1J_{SiF}$ = 109 Hz). IR (Nujol): ν = 735 (vs, br), 473 (s, br) (SiF_6) cm^{-1}. Slow evaporation of a portion of the reaction mixture yielded colourless crystals of $[\{Pb(phen)_2(SiF_6)\}_2]\cdot[Pb(phen)_2(H_2O)_2(SiF_6)]\cdot 11H_2O$.

3.5. [Pb(terpy)(SiF$_6$)]

A solution of 2,2′:6′,2″-terpyridyl (0.061 g, 0.26 mmol) in CH_3CN (5 mL) was added to $Pb(SiF_6)\cdot 2H_2O$ (0.100 g, 0.26 mmol) dissolved in deionised water (15 mL), giving a pale yellow solution. The reaction mixture was stirred for 1.5 h, then the solvent was removed *in vacuo* to yield a beige powder, which was washed with Et_2O (5 mL) and dried *in vacuo*. Yield: 0.075 g, 49%. *Anal.* Calc. for $C_{15}H_{11}F_6N_3PbSi$: C, 30.9; H, 1.9; N, 7.2. Found: C, 30.8; H, 1.8; N, 7.1%. ^1H NMR (D_2O, 295 K): δ = 7.89 (t, [2H]), 8.29 (t, [2H]), 8.50 (t, [1H]), 8.55 (d, [2H]), 8.62 (d, [2H]), 8.91 (d, 2H). $^{19}F\{^1H\}$ NMR (D_2O, 295 K): δ = −129.8 (s, $^1J_{SiF}$ = 109 Hz). IR (Nujol): ν = 716 (vs, br), 469 (s, br) (SiF_6) cm^{-1}. Slow evaporation of a portion of the reaction mixture yielded colourless crystals of $[Pb(terpy)(H_2O)(SiF_6)]$.

3.6. [Pb(terpy)$_3$][BF$_4$]$_2$

To $Pb(BF_4)_2$ as a 50% aqueous solution (0.201 g, 0.26 mmol) in deionised water (5 mL) was added a few crystals of basic lead carbonate. The resulting colourless solution was stirred for 15 min, filtered and 2,2′:6′,2″-terpyridyl (0.061 g, 0.26 mmol) in CH_3CN (5 mL) added. The colourless reaction mixture was stirred for 1.5 h, then the CH_3CN was removed *in vacuo* which caused the precipitation of a white solid. The solid was isolated by filtration, washed with Et_2O (3 mL) and dried *in vacuo*. Yield: 0.028 g, 30%. *Anal.* Calc. for $C_{45}H_{33}B_2F_8N_9Pb$: C, 50.0; H, 3.1; N, 11.7. Found: C, 49.9; H, 3.0; N, 11.8%. ^1H NMR (CD_3CN, 295 K): δ = 7.38 (td, [2H]), 8.05 (td, [2H]), 8.35 (t, [1H]), 8.47 (d, [2H]), 8.50 (d, [2H]), 8.55 (d, [2H]). $^{19}F\{^1H\}$ NMR (CD_3CN, 295 K): δ = −151.2 (s). IR (Nujol): ν = 1049 (vs, br), 520 (m) (BF_4) cm^{-1}. Slow evaporation of a portion of the reaction mixture yielded colourless crystals of $[Pb(terpy)_3][BF_4]_2$.

3.7. X-ray crystallography

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) rotating anode generator with VHF Varimax optics (70 micron focus) with the crystal

Table 1
Crystal data and structural refinement details.[a].

Compound	$[Pb(bipy)_2(BF_4)_2 \cdot 1/4H_2O]_2$	$[Pb(bipy)_2(SiF_6)]$	$[Pb(phen)_2(BF_4)_2]$	$[\{Pb(phen)_2(SiF_6)\}_2] \cdot [Pb(phen)_2(H_2O)_2(SiF_6)] \cdot 11H_2O$	$[Pb(terpy)(H_2O)(SiF_6)]$
Formula	$C_{20}H_{16.50}B_2F_8N_4O_{0.25}Pb$	$C_{20}H_{16}N_4PbSiF_6$	$C_{24}H_{16}B_2F_8N_4Pb$	$C_{72}H_{74}F_{18}N_{12}O_{13}Pb_3Si_3$	$C_{15}H_{13}F_6N_3OPbSi$
M	697.68	661.65	741.22	2363.27	600.56
Crystal system	triclinic	monoclinic	triclinic	monoclinic	triclinic
Space group (No.)	$P\bar{1}$ (No. 2)	$P2_1/n$ (No. 14)	$P\bar{1}$ (No. 2)	$P2_1/c$ (No. 14)	$P\bar{1}$ (No. 2)
a (Å)	12.796(5)	10.748(13)	7.830(5)	12.289(3)	6.938(4)
b (Å)	12.894(5)	14.188(16)	11.971(7)	31.837(6)	8.888(5)
c (Å)	13.958(5)	13.599(15)	12.983(8)	20.399(4)	13.345(8)
α (°)	83.820(12)	90	90.592(12)	90	98.936(13)
β (°)	83.697(11)	104.037(15)	96.972(12)	100.658(4)	90.905(12)
γ (°)	83.697(11)	90	95.428(17)	90	90.119(10)
U (Å^3)	2275.7(15)	2012(4)	1202.2(13)	7844(3)	812.8(8)
Z	4	4	2	4	2
μ(Mo Kα) (mm^{-1})	7.497	8.517	7.102	6.583	10.529
F(000)	1322	1256	704	4576	564
Total number of reflections	20215	6769	10707	36217	7418
R_{int}	0.0929	0.0342	0.0185	0.0344	0.0807
Unique reflections	10140	3552	5444	17354	3709
Number of parameters restraints	635, 0	283, 0	352, 0	1090, 0	270, 136
R_1, wR_2 [$I > 2\sigma(I)$][b]	0.0721, 0.1709	0.0340, 0.0594	0.0156, 0.0313	0.0419, 0.0741	0.0621, 0.1322
R_1, wR_2 (all data)	0.0895, 0.1830	0.0413, 0.0627	0.0176, 0.0315	0.0552, 0.0795	0.0693, 0.1357

[a] Common items: T = 100 K; wavelength (Mo Kα) = 0.71073 Å; θ(max) = 27.5°.

[b] $R_1 = \sum||Fo| - |Fc||/\sum|Fo|$; $wR_2 = [\sum w(Fo^2 - Fc^2)^2/\sum wFo^2]^{1/2}$.

held at 100 K (N_2 cryostream). Structure solution and refinements were performed with either SHELX(S/L)97 or SHELX(S/L)2013 [20] 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. $[\{Pb(phen)_2(SiF_6)\}_2] \cdot [Pb(phen)_2(H_2O)_2(SiF_6)] \cdot 11H_2O$ contains 13 water molecules, but it was not possible to refine hydrogens positions that formed a consistent hydrogen bonding network. Hydrogen atoms for all water molecules were therefore omitted form the refinement, but included in the formula. $[Pb(terpy)_3][BF_4]_2$ has the cation disordered around the 3-fold axis with the coordinated terpy forming both a right and left handed spiral, each with 50% occupancy. ADPs of paired atoms were constrained to be the same. One of the BF_4 anions is disordered about the 3-fold axis, ADPs of paired atoms were constrained to be the same and distance restraints for some B–F distances were applied. $[Pb(terpy)(H_2O)(SiF_6)]$ contains an SiF_6 anion that is disordered rotationally about the coordinated F–Si–F axis. This was refined in two parts and the occupancies converged on *ca.* 50/50. Geometrical restraints (FLAT) and equal ADP constraints for paired atoms were applied.

4. Conclusions

Several new diimine complexes of the lead(II) salts, $Pb(BF_4)_2$ and $Pb(SiF_6)$, have been structurally and spectroscopically characterised. All show significant fluoroanion coordination, leading to highly irregular geometries at Pb(II). The work has demonstrated that the dianionic SiF_6^{2-} can coordinate to Pb(II) to form monomer, dimer and chain polymer complexes, involving a variety of SiF_6^{2-} coordination modes. There was no evidence for fragmentation or hydrolysis of the fluoroanions in these systems, contrasting with Pb(II) macrocyclic systems [5]. These results suggest that the stable and readily available SiF_6^{2-} merits further study as a weakly coordinating dianion in other metal systems. The dianionic charge, which results in only half as many anions needed to balance the charge, is also capable of generating different structural motifs to those found with the monoanionic fluoroanions (BF_4^-, PF_6^-, *etc.*).

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Appendix A. Supplementary data

CCDC 1015057–1015062 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.poly.2014.09.016.

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