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

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A R T I C L E   I N F O

Article history:
Received 31 July 2014
Accepted 15 September 2014
Available online 10 October 2014

Keywords:
Lead(II) Hexafluorosilicate Tetrafluoroborate Diimine Triimine

A B S T R A C T

Lead(II) tetrafluoroborate and hexafluorosilicate complexes with 2,2'-bipyridyl, 1,10-phenanthroline 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)(SiF6)2], [Pb(phen)(SiF6)2] and [Pb(bipy)(BF4)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)(BF4)2] is eight-coordinate and mononuclear with "cis" diimines and two κ2-BF4 groups. [Pb(phen)(H2O)(SiF6)2] is also mononuclear with a κ2-SiF62− group and two coordinated water molecules. Reaction of Pb(BF4)2 with 2,2':6,2'-terpyridyl gave only [Pb(terpy)(BF4)2], but Pb(SiF6)2 produced [Pb(terpy)(H2O)(SiF6)] which is a chain polymer with bridging SiF62− groups and significant π-stacking of the imine rings. The work has identified a number of coordination modes of the SiF62− 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 ClO4 or CF3SO3, such as fluorinated-arylborates or -aluminates [4]. With the majority of metal ions fluoroanions such as BF4, PF6 or SbF6 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 oxaselema-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 (κ1, κ2, or µ2), 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 (ClO4, NO3 or O2CR – etc.) [7]. The [Pb(bipy)(PF6)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 repulsions. 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(BF4)2, and solid Pb(SiF6)2·2H2O, 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 fluoride groups. Pb(SiF6)2·2H2O:6PF6 etc. [7] 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 oxaselema-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 (κ1, κ2, or µ2), 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)
which it was filtered and the filtrate used immediately. Reaction of this with terpy yielded \( [\text{Pb(terpy)}]_2[\text{BF}_4]_2 \). The reaction of \( \text{Pb(BF}_4)\_2 \) or \( \text{Pb(SiF}_6)\_2 \) with either bipy or phen (or terpy, in the case of \( \text{Pb(SiF}_6)\_2 \)) in a mixture of \( \text{H}_2\text{O} \) 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 \( [\text{Pb(bipy)}]_2[\text{SiF}_6]_2 \) (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 \( [\text{Pb(bipy)}]_2(Y)\_2 \) (\( Y = \text{ClO}_4, \text{NO}_3 \)) 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 three 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–F1\_a = 2.911(2), Pb1–F4\_a = 2.811(2), Pb1–F6\_a = 2.722(4), N1–Pb1–N2 = 64.01(16), N3–Pb1–N4 = 60.61(16).

The bulk product isolated from the reaction of \( \text{Pb(SiF}_6)\_2 \) and phen was the analogous \( [\text{Pb(phen)}]_2[\text{SiF}_6]_2 \), but the crystals grown from the solution were found to have the structure \( [\text{Pb(phen)}]_2[\text{SiF}_6]_2 \) (\( \text{Pb(phen)}_2[\text{H}_2\text{O}]_2[\text{SiF}_6]_2 \) containing two lead complexes; the dimeric \( [\text{Pb(phen)}_2[\text{SiF}_6]_2] \) and a monomer with two coordinated water molecules, \( [\text{Pb(phen)}_2[\text{H}_2\text{O}]_2[\text{SiF}_6]_2] \). 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 mononeric \( [\text{Pb(phen)}]_2(Y)\_2 \) (\( Y = \text{ClO}_4, \text{NO}_3 \)) [12] have a similar PbN4 unit and achieve eight-coordination overall when the Pb–O bonds are considered.

The structure of \( [\text{Pb(phen)}]_2[\text{H}_2\text{O}]_2[\text{SiF}_6]_2 \) (Fig. 3) reveals a discrete monomer with eight-coordinate lead, through two chelating phen molecules “cis” disposed, an asymmetrically chelating (k\(^2\)) SiF\(_6^2\) group (Pb–F = 3.272(5), 2.701(5) Å), and two water molecules. Unusually, the crystal \( [\text{Pb(phen)}_2[\text{H}_2\text{O}]_2[\text{SiF}_6]_2] \) 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 \( [\text{Pb(bipy)}]_2[\text{BF}_4]_2 \) revealed it to be a dimer, with a fractionally occupied (50%) water molecule sitting between the lead centres, i.e. \( [\text{Pb(bipy)}]_2[\text{H}_2\text{O}]_2[\text{SiF}_6]_2 \) (Fig. 4). The structure is surprisingly complicated; the PbN4 geometry is similar to that found in the other diimine complexes [10,12], but instead of there being four μ2-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 k\(^1\), one is k\(^2\), one is μ\(^2\), and the fourth one chelates (k\(^2\)) 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, \( [\text{Pb(phen)}]_2[\text{BF}_4]_2 \) 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 \( [\text{Pb(phen)}_2[\text{H}_2\text{O}]_2[\text{SiF}_6]_2] \), 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.
In summary, the core geometry of the Pb(diimine)$_2$Cl$_x$Cl$_y$Cl$_z$ 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 $\kappa^2$-coordinated to a PF$_6$ group, whilst a third PF$_6$ group is coordinated in an asymmetric $\kappa^3$ mode, and the fourth PF$_6$ $\kappa^2$-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 fluoro-silicate complex prepared in this work has the formula [Pb(terpy)(H$_2$O)(SiF$_6$)$_2$] and shows a planar N$_5$-coordinated terpy. The coordinated water is disordered above and below the PbN$_5$ 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 ($\kappa^3$ $\kappa^3$) 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 = 3.56 Å.

As mentioned above, reaction of terpy with Pb(BF$_4$)$_2$ gave [Pb(terpy)$_2$][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)$_2$][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].
The coordination modes of the BF₄⁻ and PF₆⁻ 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(BF₄)₂] 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 SiF₆²⁻ coordinated to lead. The CSD [16] shows that whilst numerous examples of SiF₆²⁻ coordinated via two trans fluorines to Zn(II) in pillared coordination networks are known [17], other coordination modes are very rare. Chelation (κ²-coordination) to Cu(II) occurs in [Cu(L(SiF₆))₂(L = pyridyl-pyrazol ligand)] [18], or to Zn(II) in [Zn(phen)₂(SiF₆)] [19]. The present work has revealed examples of SiF₆²⁻ κ²-coordinated to a single lead(II) in [Pb(phen)₂(H₂O)₂(SiF₆)], whilst in the dinuclear complexes ([Pb(bipy)₂(SiF₆)] and [Pb(phen)₂(SiF₆)]) four of the fluorines from each SiF₆²⁻ 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)(H₂O)(SiF₆)] is complicated by the disorder present, but, depending on the coordination of the SiF₆²⁻ 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 BF₄⁻ and SiF₆²⁻ 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 (CD₃CN or D₂O
solution) show the imine resonances shifted to high frequency, consistent with coordination, but the $^{19}F\{^1\}H$ 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$_2$Cl$_2$). 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 $^{19}F\{^1\}H$ NMR spectra were recorded using a Bruker DPX-400 spectrometer and referenced to the residual solvent resonance and external CFC$_3$ respectively. Microanalytical measurements were performed by London Metropolitan University.

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

A solution of 2,2'-bipyridyl (0.081 g, 0.52 mmol) in CH$_2$CN (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. The solvent was removed in vacuo to yield a pale pink powder, which was washed with Et$_2$O (5 mL) and dried in vacuo. Yield: 0.113 g, 60%. Anal. Calc. for C$_{20}$H$_{18}$F$_{6}$N$_{2}$Pb: C, 34.7; H, 2.3; N, 8.1. Found: C, 34.7; H, 2.4; N, 8.2%. $^1H$ NMR (CD$_3$O, 295 K): $\delta$ = 7.78 (ddd, [2H]), 8.29 (td, [2H]), 8.42 (d, [2H]), 8.74 (dd, [2H]). $^{19}F\{^1\}H$ NMR (CD$_3$O, 295 K): $\delta$ = −150.6 (s). IR (Nujol): $\nu$ = 735 (vs, br), 473 (s) (SiF$_4$) cm$^{-1}$. Slow evaporation of a portion of the reaction mixture yielded colourless crystals of [Pb(bipy)$_2$(BF$_4$)$_2$].

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

A solution of 2,2'-bipyridyl (0.081 g, 0.52 mmol) in CH$_2$CN (5 mL) was added to Pb(SiF$_6$)$_2$(H$_2$O) (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$_2$O (5 mL) and dried in vacuo. Yield: 0.075 g, 45%. Anal. Calc. for C$_{28}$H$_{20}$F$_{12}$N$_{2}$Pb: C, 30.9; H, 1.9; N, 7.2. Found: C, 30.8; H, 1.8; N, 7.1%. $^1H$ NMR (D$_2$O, 295 K): $\delta$ = 7.89 (t, [2H]), 8.29 (t, [2H]), 8.50 (t, [1H]), 8.55 (d, [2H]), 8.62 (d, [2H]), 8.91 (d, [2H]). $^{19}F\{^1\}H$ NMR (D$_2$O, 295 K): $\delta$ = −129.7 (s, J$_{SiF}$ = 109 Hz). IR (Nujol): $\nu$ = 716 (vs, br), 469 (s) (SiF$_4$) cm$^{-1}$. Slow evaporation of a portion of the reaction mixture yielded colourless crystals of [Pb(bipy)$_2$(SiF$_6$)$_2$].

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

A solution of 1,10-phenanthroline (0.100 g, 0.55 mmol) in CH$_2$CN (5 mL) was added to Pb(SiF$_6$)$_2$(H$_2$O) (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$_2$Cl$_2$ and dried in vacuo.

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

A solution of 2.2':6.2''-terpyridyl (0.061 g, 0.26 mmol) in CH$_2$CN (5 mL) was added to Pb(SiF$_6$)$_2$(H$_2$O) (0.100 g, 0.26 mmol) dissolved in deionised water (15 mL), giving a pale yellow solid. The reaction mixture was stirred for 1.5 h, then the solvent was removed in vacuo. The resulting colourless solution was stirred for 15 min, filtered and 2.2':6.2''-terpyridyl (0.061 g, 0.26 mmol) in CH$_2$CN (5 mL) added. The reaction mixture was stirred for 1.5 h, then the CH$_2$CN was removed in vacuo to cause the precipitation of a white solid. The isolated product was washed with Et$_2$O (3 mL) and dried in vacuo. Yield: 0.028 g, 30%. Anal. Calc. for C$_{45}$H$_{32}$F$_{12}$N$_{2}$Pb: C, 50.0; H, 3.1; N, 11.7. Found: C, 49.9; H, 3.0; N, 11.8%. $^1H$ NMR (CD$_3$O, 295 K): $\delta$ = 7.38 (td, [2H]), 8.05 (td, [2H]), 8.35 (t, [1H]), 8.47 (d, [2H]), 8.50 (d, [2H]), 8.55 (d, [2H]). $^{19}F\{^1\}H$ NMR (CD$_3$O, 295 K): $\delta$ = −151.2 (s). IR (Nujol): $\nu$ = 1049 (vs, br), 520 (m) (BF$_4$) cm$^{-1}$. Slow evaporation of a portion of the reaction mixture yielded colourless crystals of [Pb(terpy)(H$_2$O)(SiF$_6$)$_2$].

3.5. [Pb(terpy)(SiF$_6$)$_2$]

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$_2$CN (5 mL) added. The reaction mixture was stirred for 1.5 h, then the CH$_2$CN was removed in vacuo to cause the precipitation of a white solid. The isolated product was washed with Et$_2$O (3 mL) and dried in vacuo. Yield: 0.028 g, 30%. Anal. Calc. for C$_{45}$H$_{32}$F$_{12}$N$_{2}$Pb: C, 50.0; H, 3.1; N, 11.7. Found: C, 49.9; H, 3.0; N, 11.8%. $^1H$ NMR (CD$_3$O, 295 K): $\delta$ = 7.38 (td, [2H]), 8.05 (td, [2H]), 8.35 (t, [1H]), 8.47 (d, [2H]), 8.50 (d, [2H]), 8.55 (d, [2H]). $^{19}F\{^1\}H$ NMR (CD$_3$O, 295 K): $\delta$ = −151.2 (s). IR (Nujol): $\nu$ = 1049 (vs, br), 520 (m) (BF$_4$) cm$^{-1}$. Slow evaporation of a portion of the reaction mixture yielded colourless crystals of [Pb(terpy)(H$_2$O)(SiF$_6$)$_2$].

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

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

### Table 1

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<td>μ(Mo Kα) (mm$^{-1}$)</td>
<td>7.497</td>
<td>8.517</td>
<td>7.102</td>
<td>6.583</td>
<td>10.529</td>
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<tr>
<td>R(000)</td>
<td>1322</td>
<td>1256</td>
<td>704</td>
<td>4576</td>
<td>564</td>
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<tr>
<td>Total number of reflections</td>
<td>20215</td>
<td>6769</td>
<td>10707</td>
<td>36217</td>
<td>7418</td>
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### Acknowledgements

We thank EPSRC for support under a programme grant (EP/I033394/1). The SCFED Project (www.sfed.net) is a multidisciplinary collaboration of British universities investigating the fundamental and applied aspects of supercritical fluids.

### 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.

### References