

# Hexafluoropentanedionatosilver(I) complexes stabilised by multidentate N-donor ligands: crystal structure of a charge-separated salt species soluble in supercritical carbon dioxide †

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A tetrahydrofuran suspension of silver(I) oxide reacted with Hhfpd (1,1,1,5,5,5-hexafluoropentane-2,4-dione) to give *in situ* [Ag(hfpd)]' after removal of the solvent *in vacuo*. Addition of equimolar ratios of multidentate amines to toluene solutions of the [Ag(hfpd)]' led to the isolation of several hexafluoropentanedionatosilver(I) complexes, [Ag(hfpd)(L-L)] [L-L = Me<sub>2</sub>NCH<sub>2</sub>CH<sub>2</sub>NHMe (trimen) **1**, Me<sub>2</sub>N(CH<sub>2</sub>)<sub>2</sub>NMe(CH<sub>2</sub>)<sub>2</sub>NMe<sub>2</sub> (pmdien) **2** or Me<sub>2</sub>N(CH<sub>2</sub>)<sub>2</sub>NMe(CH<sub>2</sub>)<sub>2</sub>NMe(CH<sub>2</sub>)<sub>2</sub>NMe<sub>2</sub> (hmten) **3**]. Addition of only half a molar equivalent of hmten to a toluene solution of [Ag(hfpd)]' led to the synthesis of [Ag(hmten)][Ag(hfpd)<sub>2</sub>] **4**. The products have been characterised by a variety of methods including microanalysis, IR, <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy and mass spectrometry and all complexes dissolve readily in supercritical carbon dioxide. Complexes **2** and **4** have been further characterised by X-ray crystallography. The structure of **2** contains a monomeric five-co-ordinate silver(I) cation in which the two chelating oxygens and two of the three amine nitrogens are in an almost planar arrangement. In comparison, the structure of **4** reveals a charge-separated salt; one of the silver atoms is exclusively co-ordinated to two hfpd ligands in a pseudo-tetrahedral arrangement, whilst the other is encapsulated by an hmten molecule.

β-Diketonate complexes of copper(I) and silver(I) have recently undergone a resurgence of interest as a result of their potential application as metal organic chemical vapour deposition (MOCVD) precursors to thin films of Cu and Ag respectively.<sup>1</sup> The general requirements for CVD precursors of these metals include good shelf life, high volatility, thermal and air/moisture stability at room temperature and decomposition to the metal at relatively low temperatures.<sup>1</sup> With the emergence of new techniques such as aerosol-assisted (AA) CVD,<sup>2,3</sup> spray pyrolysis,<sup>4</sup> spray MOCVD<sup>5</sup> and supercritical fluid transport (SFT) CVD,<sup>6,7</sup> which can overcome delivery problems caused by poor volatility, attention is now focusing on tailoring precursors which are more amenable to these new delivery methods. For example, in the SFTCVD process, good solubility in the supercritical fluid and stability in 'solution' are important factors to ensure good transfer rates are achieved.<sup>6</sup>

It has been observed that fluorinated substituents on the ligands bound to the metals tend to confer greater solubility in supercritical carbon dioxide compared with their non-fluorinated analogues.<sup>8-12</sup> Furthermore, there have recently been several reports of the solubilisation/extraction of metals in supercritical fluids using chelating agents.<sup>13-17</sup> This suggests that co-ordination of fluorinated β-diketonate ligands and (neutral) multidentate chelating co-ligands should impart to the complex excellent solubility properties in supercritical carbon dioxide.

This work is part of a broader programme in which we are preparing metal oxide/polymer composite materials by supercritical infusion of a soluble metal-organic compound into a polymer. Here we report the synthesis of several hexafluoropentanedionatosilver(I) compounds stabilised by neutral multidentate amine ligands (L-L), and which are soluble in supercritical carbon dioxide (scCO<sub>2</sub>). We envisage that the combination of a fluorinated β-diketonate ligand and neutral multidentate N-donor co-ligand(s) with silver(I) should result in saturation of

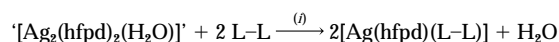
the metal co-ordination sphere, whilst retaining a relatively strong Ag-O (β-diketonate) bond.

## Results and Discussion

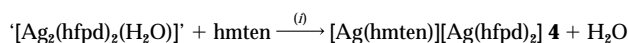
### Synthesis

The reaction of silver(I) oxide with 1,1,1,5,5,5-hexafluoropentane-2,4-dione (Hhfpd) in diethyl ether at -20 °C is known to produce a compound with limited stability at room temperature.<sup>18,19</sup> A crystal structure determination showed that this product exists as the dimer [Ag<sub>2</sub>(hfpd)<sub>2</sub>(H<sub>2</sub>O)],<sup>18</sup> which is a convenient starting material for the synthesis of the amine adducts reported herein. It was synthesized from the reaction of silver(I) oxide [suspended in tetrahydrofuran (thf) rather than diethyl ether] and Hhfpd. Following the removal of all the thf and dissolution in toluene, addition of the amine (L-L) gave a slightly exothermic reaction (Scheme 1). In the case of the four nitrogen-donor ligand Me<sub>2</sub>N(CH<sub>2</sub>)<sub>2</sub>NMe(CH<sub>2</sub>)<sub>2</sub>NMe(CH<sub>2</sub>)<sub>2</sub>NMe<sub>2</sub> (hmten) the reaction was also performed with a 1 : 2 ratio of amine : silver to give [Ag(hmten)][Ag(hfpd)<sub>2</sub>] **4**.

By adding the amine to the *in situ* [Ag<sub>2</sub>(hfpd)<sub>2</sub>(H<sub>2</sub>O)]' rather than to the reactant mixture we avoided pre-reaction of the amine prior to co-ordination. Addition of the amines at the start of the reactions led to more vigorous exothermic reactions and greater quantities of filtered Ag<sub>2</sub>O (indicating lower yields) than were observed for the preferred route described above and in the Experimental section. We suspect that the exothermic reaction is due to proton-transfer reactions involving



L-L = trimen **1**, pmdien **2** or hmten **3**



**Scheme 1** (i) Toluene, 25 °C, trimen = Me<sub>2</sub>NCH<sub>2</sub>CH<sub>2</sub>NHMe, pmdien = Me<sub>2</sub>N(CH<sub>2</sub>)<sub>2</sub>NMe(CH<sub>2</sub>)<sub>2</sub>NMe<sub>2</sub>, hmten = Me<sub>2</sub>N(CH<sub>2</sub>)<sub>2</sub>NMe(CH<sub>2</sub>)<sub>2</sub>NMe(CH<sub>2</sub>)<sub>2</sub>NMe<sub>2</sub>

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‡ Non-SI units employed: psi ≈ 6895 Pa; Torr ≈ 133 Pa.

**Table 1** Proton-1 NMR chemical shifts ( $\delta$ ) for complexes **1–4** in  $\text{CDCl}_3$ 

Compound	NMe <sub>2</sub>	NMe	CH <sub>2</sub>	CH <sub>2</sub>	CH
<b>1</b> *	2.41 (s, 6 H)	2.63 (s, 3 H)	2.53 (m, 2 H)	2.78 (m, 2 H)	5.77 (s, H)
<b>2</b>	2.32	2.32 (s, 15 H)	2.42 (m, 4 H)	2.49 (m, 4 H)	5.65 (s, H)
<b>3</b>	2.38 (6 H)	2.44 (s, 12 H)	2.52	2.52 (m, 12 H)	5.58 (s, H)
<b>4</b>	2.40 (3 H)	2.54 (s, 6 H)	2.60	2.60 (m, 6 H)	5.65 (s, H)

\*  $\delta$  3.05 (s, br, 1 H, NH).

**Table 2** Carbon-13 NMR chemical shifts ( $\delta$ ) for complexes **1–4** in  $\text{CDCl}_3$ 

Compound	NMe	NMe <sub>2</sub>	CH <sub>2</sub>	CH	CF <sub>3</sub>	CO
<b>1</b>	39.6	47.7	49.8, 60.2	86.4	117.8 (q)	176.5 (q)
<b>2</b>	44.2	47.2	55.1, 58.0	84.8	118.0 (q)	175.2 (q)
<b>3</b>	44.0	48.5	55.7, 59.1	84.4	117.1 (q)	175.0 (q)
<b>4</b>	44.3	49.4	55.4, * 59.7	86.3	117.8 (q)	176.4 (q)

\* Also  $\delta$  56.0.

the amine ligands. A similar reaction between the Group 2 metal ethoxide [ $\{\text{Sr}(\text{OEt})_2(\text{EtOH})_4\}_n$ ] with tmen (*N,N,N'*-tetramethylethane-1,2-diamine) and the fluorinated ligand Htfpd (1,1,1-trifluoropentane-2,4-dione) led to protonation of the Lewis-base multidentate amine ligands and the formation of the tight cation–anion pair  $[\text{Htmten}]_2[\text{Sr}(\text{tfpd})_4]$  in low yield.<sup>20</sup>

Our synthetic strategies are similar to those employed for the preparation of the related multidentate O- and N-donor stabilised Group 2 and lanthanide  $\beta$ -diketonate complexes.<sup>21–27</sup> In those cases it was observed that the smaller amines afforded monomeric complexes such as  $[\text{Ca}(\text{dppd})_2(\text{pmdien})]^{27}$  (Hdppd = 1,3-diphenylpropane-1,3-dione) while a 1:2 ratio of polyether ligand:metal (lanthanide) gave rise to bridged complexes such as  $[\{\text{Gd}(\text{tmhd})_3\}_2(\text{tetraglyme})]$  [Htmhd = 2,2,6,6-tetramethylheptane-3,5-dione; tetraglyme =  $\text{CH}_3\text{O}(\text{CH}_2\text{CH}_2\text{O})_4\text{CH}_3$ ],<sup>24</sup>  $[\{\text{Ce}(\text{etfa})_3\}_2(\text{tetraglyme})]^{25}$  (etfa = ethoxytrifluoroacetylacetonate) and  $[\{\text{Er}(\text{tmhd})_3\}_2(\text{tetraglyme})]^{26}$ .

### Physical properties

All the compounds have good solubility in an extensive range of organic solvents, especially in co-ordinating solvents such as ethers (*i.e.* thf and diethyl ether) and in aromatics. The complexes show poor to moderate solubilities in *n*-hexane. Solubility of all the complexes in  $\text{scCO}_2$  [40–50 °C, *ca.* 2500 psi] was demonstrated by qualitative solubility/impregnation tests in which the compounds were dissolved in  $\text{scCO}_2$  and infused into a polymer (see general procedures in Experimental section). The excellent solubility properties of the complexes is most likely to be due to the metals being surrounded by an organic (hydrophobic) exterior and to the highly fluorinated side-groups of the hfpd ligands which reduce van der Waals interactions.

The complexes are slightly light and air sensitive, decomposing slowly over a few days in air. The pmdien adduct  $[\text{Ag}(\text{hfpd})(\text{pmdien})]$  **2** melts at slightly above room temperature in the range 34–36 °C. In contrast, the complex  $[\text{Ag}(\text{hfpd})(\text{trimen})]$  **1** does not melt but decomposes above 80 °C. The hmten adduct  $[\text{Ag}(\text{hfpd})(\text{hmten})]$  **3** melts between 71 and 75 °C, whilst the related charge-separated salt  $[\text{Ag}(\text{hmten})][\text{Ag}(\text{hfpd})_2]$  **4** melts in the slightly lower temperature range 65–71 °C.

To determine whether any of these silver(I) compounds were volatile, we attempted to sublime the complexes in the temperature range 80–110 °C ( $1 \times 10^{-2}$  Torr). Complexes **2** and **3** were observed to sublime quantitatively under these conditions, whilst **1** and **4** decomposed to give black residues.

### Spectroscopic studies

The infrared spectra of complexes **1–4** were studied as Nujol mulls between KBr discs, and for **2** in supercritical  $\text{CO}_2$  using a

high-pressure cell with  $\text{CaF}_2$  windows. The IR bands are assigned on the basis of data for previously characterised  $\beta$ -diketonate complexes.<sup>21,22,28,29</sup> The spectra showed a single band in the region 1670–1633  $\text{cm}^{-1}$ , which was assigned as a  $\nu(\text{C}=\text{O})$  stretch of the hfpd ligands. Furthermore,  $\nu(\text{C}=\text{C})$  stretching modes of the hfpd ligands were observed in the range 1533–1512  $\text{cm}^{-1}$ .

The  $^1\text{H}$  and  $^{13}\text{C}$  NMR data are in accord with the proposed molecular formulae. The spectra for compounds **1–4** reveal two distinct methyl signals for the amine ligands (Tables 1 and 2 respectively). Complexes **1** and **2** show two distinct methylene multiplets, whilst for **3** and **4** these sets of peaks are superimposed. The  $^1\text{H}$  NMR spectra for complexes **1–4** reveal a single CH peak for the hfpd ligand in the range  $\delta$  5.58–5.77 ( $^{13}\text{C}$  NMR range of  $\delta$  84.4–86.4). The spectrum for complex **1** also contains a peak at  $\delta$  3.05 due to the NH hydrogen of the trimen ligand.

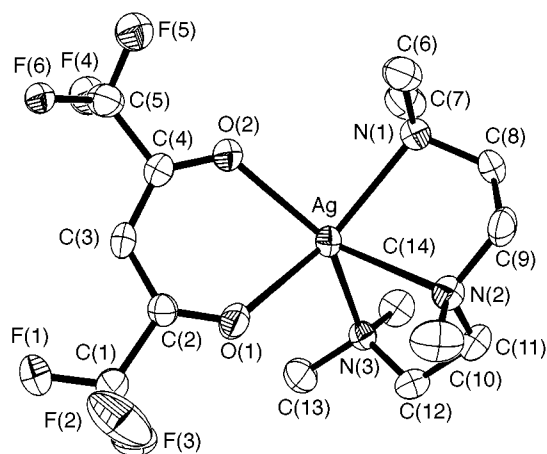
All the  $^{13}\text{C}$  NMR spectra (Table 2) exhibit two sets of quartets for the  $\beta$ -diketonate ligands: the first set due to the  $\text{CF}_3$  carbon is observed in the narrow range  $\delta$  117.1–118.0, and the second set due to the CO carbon lies in the range  $\delta$  175.0–176.5. Two peaks corresponding to the methylene carbons of the amine ligands are observed in the  $^{13}\text{C}$  NMR spectra of complexes **1** and **2** in the range  $\delta$  49.8–60.2. The  $^{13}\text{C}$  NMR spectra for complexes **3** and **4** reveal two and three  $\text{CH}_2$  peaks, respectively, for the hmten ligand. This suggests that the hmten ligand is possibly more strongly held in **4**, giving distinctly differing  $\text{CH}_2$  environments and is therefore less likely to be undergoing exchange processes in solution.

Mass spectra for all the complexes were obtained in the positive-ion fast atom bombardment (FAB) mode and revealed peaks corresponding to the respective  $[\text{Ag}(\text{L-L})]^+$  (L-L = amine ligand) molecular ions as well as the  $[\text{L-L}]^+$  ion. All the spectra also contained peaks at lower *m/z* corresponding to fragmented amine ligands.

### Crystal structure of $[\text{Ag}(\text{hfpd})(\text{pmdien})]$ **2**

A crystal structure determination of complex **2** showed that it is monomeric, in agreement with the spectroscopic data. The complex (Fig. 1) contains a five-co-ordinate silver atom bonded to a chelating hfpd ligand and a tridentate pmdien ligand. The overall co-ordination polyhedron may be described as a severely distorted square-based pyramid, with the two chelating hfpd oxygens [O(1) and O(2)] and two of the three amine nitrogens [N(1) and N(2)] forming the basal plane, and the third (terminal) nitrogen N(3) located at the apex of the pyramid. The silver atom is 0.746 Å out of the mean basal plane in the direction of N(3).

The Ag–O (hfpd) bond lengths [2.419(4) and 2.376(4) Å] (Table 3) are comparable to those observed for other silver(I)



**Fig. 1** Structure of  $[\text{Ag}(\text{hfpd})(\text{pmdien})]$  **2**, only one orientation of the disordered  $\text{CF}_3$  group is shown. Thermal ellipsoids are drawn at 50% probability level; H atoms have been omitted for clarity

complexes involving purely chelating hfpd ligands, e.g. 2.402, 2.477 Å in  $[\text{Ag}(\text{hfpd})_2(\text{ots})_2]$ , (ots = 1,4-oxathiane),<sup>18</sup> 2.330, 2.330 Å in  $[\text{Ag}(\text{hfpd})_2(\text{SEt}_2)]$ ,<sup>19,30</sup> and 2.282, 2.301 Å in  $[\text{Ag}(\text{hfpd})_2(\text{PMe}_3)_2]$ ,<sup>31,32</sup> but the bonds are not asymmetric as observed for  $[\text{Ag}(\text{hfpd})_2(\text{PMe}_3)_2]$  (2.450 and 2.642 Å).<sup>31</sup> The distances in **2** are also similar to those observed in the chelating/bridging hfpd ligands in  $[\text{Ag}_2(\text{hfpd})_2(\text{H}_2\text{O})]$  (2.346, 2.419, 2.414, 2.400, 2.442 and 2.415 Å),<sup>18</sup> and considerably shorter than those observed for  $[\text{Ag}_2(\text{hfpd})_2(\text{cod})_2]$  (cod = cycloocta-1,5-diene) (2.508, 2.579, 2.559, 2.541, 2.468 and 2.446 Å)<sup>33</sup> and  $[\text{Ag}_2(\text{hfpd})_2(\text{Me}_2\text{PCH}_2\text{PMe}_2)_2]$  (2.692, 2.528, 2.528 and 2.692 Å).<sup>34</sup>

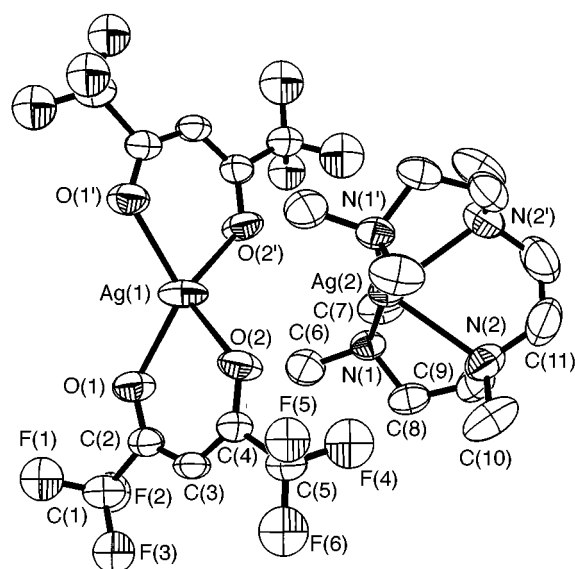
The Ag–N bond lengths of the pm dien complex are found to lie in the narrow range 2.421(5)–2.455(5) Å. The average (2.442 Å) is only ca. 0.04 Å longer than the average Ag–O (hfpd) distance (2.398 Å), which suggests relatively strong Ag–N bonds. The structure of complex **2** can be compared to a recently characterised monomeric complex  $[\text{Ag}(\text{hfpd})(\text{tetraglyme})]$ <sup>35</sup> in which an  $\text{Ag}(\text{hfpd})$  moiety is co-ordinated to four out of the five oxygens of the polyether ligand. In the glyme adduct the average Ag–O (tetraglyme) distance is approximately 0.16 Å longer than the average Ag–N (pmdien) distance observed in compound **2**, which suggests that the N-donor ligand possibly provides a better ligand match with the silver cations than does tetraglyme.

### Crystal structure of $[\text{Ag}(\text{hfpd})(\text{hmt en})]$ **3**

A single-crystal X-ray study of complex **3** confirmed that it is monomeric as expected. The complex contains a six-coordinate silver atom which is bonded to four nitrogen and two oxygen atoms of a hmt en and hfpd ligand respectively. Although the gross structure has been established, the presence of extensive disorder precludes meaningful discussion of the molecular geometry.†

### Crystal structure of $[\text{Ag}(\text{hmt en})][\text{Ag}(\text{hfpd})_2]$ **4**

As a consequence of the 1:2 stoichiometry of hmt en:silver employed in the synthesis of this complex,  $[\text{Ag}(\text{hmt en})][\text{Ag}(\text{hfpd})_2]$  **4** crystallises as a charge-separated salt with four-coordinate silver atoms (Fig. 2). One of the silver atoms  $[\text{Ag}(1)]$  is co-ordinated exclusively to four oxygens from two hfpd ligands in a pseudo-tetrahedral arrangement, whilst the other  $[\text{Ag}(2)]$  is partially encapsulated by four nitrogens  $[\text{N}(1)$ ,



**Fig. 2** Structure of  $[\text{Ag}(\text{hmt en})][\text{Ag}(\text{hfpd})_2]$  **4**, showing the atomic numbering scheme and thermal ellipsoids drawn at 50% probability level. Primed atoms are related to unprimed equivalents by the symmetry operation  $1 - x, y, \frac{1}{2} - z$ . Only one orientation of the disordered  $\text{CF}_3$  group is shown; H atoms have been omitted for clarity

**Table 3** Selected bond lengths (Å) and angles (°) for  $[\text{Ag}(\text{hfpd})(\text{pmdien})]$  **2**

Ag–O(1)	2.419(4)	Ag–N(2)	2.455(5)
Ag–O(2)	2.376(4)	Ag–N(3)	2.421(5)
Ag–N(1)	2.450(5)		
O(1)–Ag–O(2)	76.7(1)	O(2)–Ag–N(2)	140.0(2)
O(1)–Ag–N(1)	147.5(2)	O(2)–Ag–N(3)	142.1(2)
O(1)–Ag–N(2)	98.0(2)	N(1)–Ag–N(2)	75.3(2)
O(1)–Ag–N(3)	94.3(2)	N(1)–Ag–N(3)	114.5(2)
O(2)–Ag–N(1)	88.3(2)	N(2)–Ag–N(3)	77.3(2)

**Table 4** Selected bond lengths (Å) and angles (°) for  $[\text{Ag}(\text{hmt en})][\text{Ag}(\text{hfpd})_2]$  **4**

Ag(1)–O(1)	2.292(6)	Ag(2)–N(1)	2.258(7)
Ag(1)–O(2)	2.327(6)	Ag(2)–N(2)	2.530(8)
O(1')–Ag(1)–O(1)	123.6(3)	N(1')–Ag(2)–N(1)	164.2(4)
O(1')–Ag(1)–O(2)	130.8(2)	N(1')–Ag(2)–N(2)	114.6(3)
O(1)–Ag(1)–O(2)	80.7(2)	N(1)–Ag(2)–N(2)	78.8(3)
O(2)–Ag(1)–O(2')	117.1(3)	N(2)–Ag(2)–N(2')	71.9(4)
Ag(1)–O(1)–C(2)	127.1(5)		

Symmetry operation:  $1 - x, y, \frac{1}{2} - z$ .

$\text{N}(2)$ ,  $\text{N}(2')$  and  $\text{N}(1')$ ] from a single hmt en molecule to give an approximate octahedral geometry with two vacant equatorial sites (saw-horse arrangement). The overall molecule has crystallographic  $C_2$  symmetry with the two silver atoms lying on the two-fold axis.

The Ag–O (hfpd) bond lengths are 2.292(6) and 2.327(6) Å (Table 4), slightly shorter than those observed in compound **2**. The O–Ag–O bite angles of the hfpd ligands are relatively large  $[80.7(2)^\circ]$  and can be compared to  $76.65(14)^\circ$  for complex **2** and the range  $73.5$ – $76.8^\circ$  for other hfpd ligands co-ordinated to silver atoms.<sup>18</sup> This can be viewed as a compromise between increased strain in the ' $\text{AgO}_2\text{C}_3$ ' rings and the need to stabilise the metal centre with only four oxygens from the two hfpd ligands. Distortions of the oxygen co-ordination sphere of  $\text{Ag}(1)$  from an idealised tetrahedron (ca.  $109.5^\circ$ ) are reflected in the remaining O–Ag–O bond angles of  $130.8(2)$  (twice) and  $123.6(3)^\circ$  (twice).

† Crystal data.  $\text{C}_{17}\text{H}_{31}\text{AgF}_6\text{N}_4\text{O}_2$  **3**,  $M = 544.32$ , yellow block ( $0.34 \times 0.32 \times 0.14$  mm), monoclinic, space group  $Cc$ ,  $a = 13.370(8)$ ,  $b = 10.484(2)$ ,  $c = 17.744(3)$  Å,  $\beta = 107.91(2)^\circ$ ,  $U = 2366.6(11)$  Å<sup>3</sup>,  $Z = 4$ ,  $F(000) = 1108$ ,  $D_c = 1.528$  g cm<sup>-3</sup>,  $\mu(\text{Mo-K}\alpha) = 0.92$  mm<sup>-1</sup>.

The bonding of the hmten ligand to Ag(2) results in extremely short Ag–N (hmten) bonds at the terminal N atoms Ag(2)–N(1) [2.258(7) Å] and rather longer distances for the two central nitrogens Ag(2)–N(2) [2.530(8) Å]. The interbond angles show clearly that the co-ordination sphere of Ag(2) is severely distorted from the idealised 'saw-horse' geometry. The angle N(1)–Ag(2)–N(1') which involves the two terminal (axial) nitrogens is 164.2(4)° and lies far from linearity. The angles between the terminal (axial) and central (equatorial) nitrogens N(1)–Ag(2)–N(2) and N(1')–Ag(2)–N(2) are 78.8(3) and 114.6(3)° respectively, and the angle between the two central (equatorial) nitrogens of the hmten ligand N(2)–Ag(2)–N(2') is 71.9(4)° rather than 90° which would be expected for the idealised saw-horse geometry.

Although the open face of Ag(2) points in the general direction of Ag(1) the two ions do not interact significantly [Ag(1)···Ag(2) 4.241(6) Å]. The nearest non-bonding distance involving the silver atoms is 3.620(6) Å for Ag(2)···O(2), well in excess of the corresponding van der Waals radii sum of *ca.* 2.35 Å.<sup>36</sup>

## Conclusion

The new hexafluoropentanedionatosilver(i) adducts of multi-dentate N-chelates synthesized and characterised here, have been obtained in reasonable yields and show limited stability in air. As envisaged, careful control of the ligand stoichiometry has led to a change in the molecularity of the product. The formation of the charge-separated species **4**, rather than a much larger aggregate, is attributed to the ease with which the co-ordination requirements of silver can be satisfied. This work has demonstrated that the apparently poor match of a 'soft' Lewis acid and 'hard' donor ligands has nevertheless led to complexation of the amines in all cases. The N-donor ligands used would not be expected to provide a good match for a silver(i) cation. However, the X-ray crystal data and mass spectra for complexes **2** and **4** suggest fairly strong Ag–N bonds. Furthermore, the silver– $\beta$ -diketonate bonds are in the region of *ca.* 2.4 Å, suggesting that the hfpd ligands are also strongly co-ordinated.

The solubilisation of the charge-separated compound **4** in scCO<sub>2</sub> was rather surprising given the apparently poor solvating properties associated with this medium (believed to be akin to solvents such as *n*-hexane or pentane). This suggests that it may also be possible to dissolve heterometallic complexes in scCO<sub>2</sub> provided that there are sufficient fluorinated/chelating ligands present in the molecule. This could furnish a mechanism for 'molecular level' dispersion of two different metal oxides into a polymer *via* supercritical infusion of a heterometallic precursor. We are currently testing the solubilities of a range of heterometallic complexes in scCO<sub>2</sub> and exploiting the excellent solubilities of the compounds reported here, for the preparation of supercritically infused composite metal oxide/polymer materials.

## Experimental

### General procedures

All reactants and products were manipulated under a nitrogen atmosphere (Schlenk line), argon atmosphere (glove-box) or *in vacuo*, with exclusion of moisture and air. The solvents were pre-dried then distilled prior to use, and stored over 4 Å molecular sieves under an atmosphere of nitrogen in a glass storage vessel fitted with a Young's high-vacuum PTFE (polytetrafluoroethylene) stopcock. Qualitative solubility/impregnation tests were performed by using supercritical carbon dioxide (40–50 °C, *ca.* 2500 psi) to infuse the compounds into ultra-high-molecular-weight polyethylene thin discs. Tests were conducted in a Thar Designs high-pressure extraction vessel (10 cm<sup>3</sup> volume, rated to 10 000 psi, 100 °C) using gaseous carbon dioxide (grade 3.5 purity) as supplied by Cryoservices Ltd.

### Instrumentation

Infrared spectra were recorded on a Nicolet 5DX FT-IR spectrometer as Nujol mulls between KBr plates, in the region 4000–400 cm<sup>-1</sup>, NMR solution spectra on a Bruker Avance DPX 300 MHz spectrometer, <sup>1</sup>H at 300.13 MHz (at 25 °C), <sup>13</sup>C-{<sup>1</sup>H} at 73.03 MHz. Chemical shifts were referenced using the protio impurities of the deuteriated solvent. Elemental analyses were performed at Nottingham by the Department of Chemistry microanalytical service. Mass spectrometric data were obtained on a VG Autospec (FAB) instrument (Nottingham) in the mode specified. Melting points were recorded in unsealed capillaries and are uncorrected.

### Starting materials

Silver(i) oxide was obtained from Aldrich and used as purchased. The compounds trimen, pmdien, hmten, and 1,1,1,5,5,5-hexafluoropentane-2,4-dione (Aldrich) were stored over 4 Å molecular sieves prior to use.

### Preparations

**[Ag(hfpd)(trimen)] 1.** Silver(i) oxide (2.24 g, 9.6 mmol) was weighed into a Schlenk tube and suspended in thf (40 cm<sup>3</sup>). The compound Hhfpd (2.70 cm<sup>3</sup>, 19.2 mmol) was added to this mixture with rapid stirring and the reaction left to stir for 30 min. During this time most of the black silver(i) oxide dissolved to yield a slightly turbid solution. The mixture was filtered through a sinter packed with Celite and glass-wool, to give a clear solution. The solvent was removed *in vacuo* to give an off-white solid. The solid was dissolved in toluene (40 cm<sup>3</sup>) and trimen (2.31 cm<sup>3</sup>, 18.2 mmol) was slowly added, whereupon an exothermic reaction occurred with the evolution of some gas, to give a brown solution. The reaction was then allowed to stir for 20 min, layered with *n*-hexane (15.0 cm<sup>3</sup>) and left at 0 °C for 12 h: this yielded a crop of colourless crystals (4.16 g, 54.9% with respect to trimen), m.p. >80 °C (decomposes to a brown oil) (Found: C, 28.90; H, 3.63; N, 6.55. C<sub>10</sub>H<sub>15</sub>AgF<sub>6</sub>N<sub>2</sub>O<sub>2</sub> requires C, 28.84; H, 3.60; N, 6.73%);  $\tilde{\nu}_{\max}/\text{cm}^{-1}$  (Nujol) 3261m, 3123w, 1668m, 1537m, 1523m, 1450s, 1251s, 1192s, 1129s, 1031m, 1009m, 965m, 929m, 842m, 784m, 726m, 654m, 567m and 516w; mass spectrum (positive-ion FAB, selected ions) *m/z* 209, [Ag(trimen)]<sup>+</sup>; 102, [trimen]<sup>+</sup>.

**[Ag(hfpd)(pmdien)] 2.** This compound was prepared using a similar method to that employed for **1**, but using pmdien (3.16 g, 18.2 mmol) instead of trimen. The solvent was removed to give a yellow oil which crystallised upon standing (3.0 g, 34% with respect to pmdien), m.p. 34–36 °C (Found: C, 35.04; H, 5.27; N, 8.90. C<sub>14</sub>H<sub>24</sub>AgF<sub>6</sub>N<sub>3</sub>O<sub>2</sub> requires C, 34.49; H, 4.92; N, 8.62%);  $\tilde{\nu}_{\max}/\text{cm}^{-1}$  (Nujol) 2836w, 1671s, 1553m, 1533s, 1300w, 1252s, 1189s, 1132s, 1026w, 930w, 779m, 656m and 567w; (sc-CO<sub>2</sub>, 1800 psi, 32.8 °C) 1663m, 1524m, 1466w, 1256m, 1199s and 1143s; mass spectrum (positive-ion FAB, selected ions) *m/z* 280, [Ag(pmdien)]<sup>+</sup>; 172, [pmdien]<sup>+</sup>.

**[Ag(hfpd)(hmten)] 3.** This compound was prepared using a similar method to that employed for **1**, but using hmten (4.96 cm<sup>3</sup>, 18.2 mmol) instead of trimen. The reaction was allowed to stir for 10 min and then layered with *n*-hexane (15.0 cm<sup>3</sup>) and left at 0 °C to give a crop of yellow crystals (5.3 g, 53% with respect to hmten), m.p. 71–75 °C (Found: C, 37.34; H, 5.94; N, 10.44. C<sub>17</sub>H<sub>31</sub>AgF<sub>6</sub>N<sub>4</sub>O<sub>2</sub> requires C, 37.56; H, 5.70; N, 10.31%);  $\tilde{\nu}_{\max}/\text{cm}^{-1}$  (Nujol) 1667s, 1646m, 1561s, 1526s, 1244s, 1174s, 1139s, 1117s, 1026w, 934w, 772w, 652w and 568w; mass spectrum (positive-ion FAB, selected ions) *m/z* 337, [Ag(hmten)]<sup>+</sup>; 231, [hmten]<sup>+</sup>.

**[Ag(hmten)][Ag(hfpd)<sub>2</sub>] 4.** This compound was prepared using a similar method to that employed for **3** except that a 2 : 1

**Table 5** Crystal data and details of data collection for [Ag(hfpd)(pmdien)] **2** and [Ag(hmten)][Ag(hfpd)<sub>2</sub>] **4**

	<b>2</b>	<b>4</b>
Formula	C <sub>14</sub> H <sub>24</sub> AgF <sub>6</sub> N <sub>3</sub> O <sub>2</sub>	C <sub>22</sub> H <sub>32</sub> Ag <sub>2</sub> F <sub>12</sub> N <sub>4</sub> O <sub>4</sub>
<i>M</i>	488.23	860.26
Crystal size/mm	0.62 × 0.23 × 0.06	0.76 × 0.54 × 0.47
Crystal system	Orthorhombic	Monoclinic
Space group	<i>Pbca</i>	<i>C2/c</i>
<i>a</i> /Å	8.799(11)	9.945(5)
<i>b</i> /Å	19.42(2)	15.716(10)
<i>c</i> /Å	22.50(3)	20.21(2)
β/°		98.89(11)
<i>U</i> /Å <sup>3</sup>	3845(8)	3121(4)
<i>Z</i>	8	4
<i>D</i> <sub>c</sub> /g cm <sup>-3</sup>	1.687	1.831
μ/mm <sup>-1</sup>	1.117	1.361
<i>F</i> (000)	1968	1704
2θ <sub>max</sub> /°	50	50
Ranges of <i>h, k, l</i>	0 to 10, 0 to 23, -26 to 26	-11 to 7, 0 to 18, 0 to 24
Measured reflections	6323	2499
Independent reflections ( <i>R</i> <sub>int</sub> )	3388 (0.0426)	2499 (—)
Observed reflections [ <i>F</i> ≥ 4σ( <i>F</i> )]	2266	2170
Absorption corrections:		
<i>T</i> <sub>min,max</sub>	0.746, 0.937 (numerical)	0.455, 0.556 (ψ scans)
Full-matrix least squares on <i>F</i> <sup>2</sup>	<i>F</i> <sup>2</sup>	<i>F</i> <sup>2</sup>
Weighting scheme coefficients <sup>38</sup>	0.0022, 9.50	0.0584, 47.1154
Parameters refined	261	197
SHELXL 96 <i>R</i> <sub>1</sub> , <i>wR</i> <sub>2</sub> , <i>S</i> <sup>38</sup>	0.0482, 0.0648, 0.120	0.0596, 0.1403, 1.054
(Δ/σ) <sub>max</sub>	0.069	0.020
Δρ <sub>max,min</sub> /e Å <sup>-3</sup>	+0.449, -0.422	+0.994, -0.877

ratio of Ag:hmten was employed. Upon the addition of hmten (2.48 cm<sup>3</sup>, 9.1 mmol) an exothermic reaction occurred with the evolution of some gas, to give a dark brown solution. The solvent volume was reduced to ca. 20 cm<sup>3</sup> and the solution was placed at -20 °C overnight. The solvent was then removed *in vacuo* and the resulting solid dissolved in toluene (20.0 cm<sup>3</sup>). This solution was slowly layered with *n*-hexane (25.0 cm<sup>3</sup>) and then kept at -20 °C for 3 h after which time brown crystals had precipitated (4.91 g, 63% with respect to hmten), m.p. 65–71 °C (Found: C, 30.57; H, 3.75; N, 6.22. C<sub>22</sub>H<sub>32</sub>Ag<sub>2</sub>F<sub>12</sub>N<sub>4</sub>O<sub>4</sub> requires C, 30.76; H, 3.72; N, 6.52%);  $\tilde{\nu}_{\max}$ /cm<sup>-1</sup> (Nujol) 3123m, 1660m, 1639m, 1537m, 1494m, 1443s, 1306m, 1255s, 1183s, 1125s, 1016m, 980m, 922m, 777m, 755m, 661m, 567m and 524w; mass spectrum (positive-ion FAB, selected ions) *m/z* 337, [Ag(hmten)]<sup>+</sup>; 231, [hmten]<sup>+</sup>.

### X-Ray crystallography

The following procedure is typical. A single crystal suitable for X-ray diffraction studies was mounted in the cold dinitrogen stream (220 K) of an Oxford Cryosystems low-temperature device<sup>37</sup> on a Stoë Stadi-4 four-circle diffractometer [graphite-monochromated Mo-Kα X-radiation (λ = 0.71073 Å); ω-θ scan mode]. Other details of crystal data, data collection and processing and structure analysis are given in Table 5. The structures of complexes **2** and **4** were solved by direct methods using SHELXS 96<sup>39</sup> and developed by alternating cycles of least-squares refinement and Δ*F* syntheses. Disorder in one of the CF<sub>3</sub> groups for complex **2** was modelled as four orientations for each F atom, with group occupation factors and with similarity restraints to C–F distances and F–C–F angles.

In complex **4** the two CF<sub>3</sub> groups had each of its F atoms disordered over two positions, with equal site occupancy of 0.5. All ordered non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were included in calculated positions riding on the parent C atom. Illustrations were generated using SHELXTL-PC,<sup>40</sup> and molecular geometry calculations utilised CALC,<sup>41</sup> SHELXTL-PC,<sup>40</sup> and SHELXL 96.<sup>38</sup>

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