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Synthesis and Properties of Polyether Adducts of Hexafluoropentanedionatosilver(I)

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A series of polyether [$CH_3O(CH_2CH_2O)_mCH_3$, with $m = 2$ (diglyme), 3 (triglyme), 4 (tetraglyme)] mono- or hemiadducts of hexafluoropentanedionatosilver(I) have been synthesized and in selected cases structurally characterized. Decomposition of [Ag(hfa)(diglyme)]$_2$ (hfa = hexafluoropentanedionato) in air affords a mixture of products including crystals of [Ag_2(hfa)(O_2CCF_3)(diglyme)$_2$]. The structure of [Ag(hfa)(diglyme)]$_2$ consists of two silver cations which are bridged by four oxygens from two hfa ligands; each Ag(I) ion is also coordinated to a chelating diglyme molecule. In comparison, ligation of a longer polyether chain results in a monomeric species [Ag(hfa)(tetraglyme)]. The compounds are soluble in a range of solvents including supercritical carbon dioxide ($scCO_2$). Crystal data for [Ag(hfa)(diglyme)]$_2$ (150 K): $a = 21.376(3)$ Å, $b = 8.4143(17)$ Å, $c = 21.067(3)$ Å, $\beta = 124.05(1)°$, monoclinic space group $C2/c$; $Z = 8$. Crystal data for [Ag_2(hfa)(O_2CCF_3)(diglyme)$_2$] (150 K): $a = 9.0945(12)$ Å, $b = 9.4110(13)$ Å, $c = 17.803(2)$ Å, $\alpha = 96.109(14)°$, $\beta = 101.649(13)°$, $\gamma = 105.06(2)°$, triclinic space group $P\bar{1}$; $Z = 2$. Crystal data for [Ag(hfa)(tetraglyme)] (150 K): $a = 14.152(3)$ Å, $b = 16.996(3)$ Å, $c = 8.620(2)$ Å, $\beta = 106.99(2)°$, monoclinic space group $P2_1/c$; $Z = 4$.

Introduction

Silver(I) and copper(I) β-diketonate complexes have received significant attention due to the ease with which they can be converted to the elemental metals by thermal decomposition techniques such as metal organic chemical vapor deposition (MOCVD).[1] The larger cationic radius of silver(I) with respect to copper(I) has, however, caused problems in achieving both good volatility and adequate stability of silver(I) complexes for use in CVD apparatus.[2−7] To some extent these problems are less important with new techniques such as SFTCVD (supercritical fluid transport CVD),[8,9] AACVD (aerosol-assisted CVD),[10,11] and spray pyrolysis,[12] where the requirements for volatile precursors are less stringent. Instead, properties such as good solubility and stability in solution and clean decomposition of the precursor become important factors. Various methods of improving these physical properties include the use of neutral coordinating ligands in the transport medium (gas phase or solution). For example, coordination of polyether (glyme) ligands to one or more metal centers has often afforded compounds with improved mass transport properties and stability compared to their unadducted analogues.[13−16] Although neutral O-donor ligands would not be expected to provide good ligand matches for a silver(I) cation, they have been selected by us in the belief that they will saturate the silver coordination sphere while encouraging strong Ag−O(β-diketonate) bonds, which are important if the compounds are to have reasonable thermal and air stability.

In this work, we describe the preparation and characterization of polyether adducts of hexafluoropentanedionatosilver(I). We have attempted to saturate the coordination sphere of the silver cation with a combination of fluorinated β-diketonate chelating ligand(s) and neutral multidentate co-ligand(s) in the hope that the products will show good solubilities and stabilities in a range of hydrocarbon solvent solvents and fluids such as supercritical carbon dioxide ($scCO_2$).

Results and Discussion

Synthesis. The reactions of Ag_2O with 2 molar equiv of H-hfa (1,1,1,5,5,5-hexafluoropentane-2,4-dione) in the presence of polyether (glyme) ligands, gave the corresponding monoadducted glyme complexes [Ag(hfa)(L−L)]$_n$ (see below). In all cases, the reaction mixtures were then filtered to remove a very small amount of finely suspended black solid, presumed to be unreacted silver(I) oxide (Scheme 1).

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Scheme 1[a]

$$Ag_2O + 2H\text{-hfa} + 2\,(L{-}L) \xrightarrow{(i), (ii), (iii)} 2[Ag(hfa)(L{-}L)]_n + H_2O$$

$$[L{-}L = \text{diglyme } (\mathbf{1}), \text{ triglyme } (\mathbf{3}), \text{ tetraglyme } (\mathbf{4})]$$

[a] Legend: (i) thf/20 °C; (ii) filter, remove solvent; (iii) toluene/−20 °C(**1**: also layer *n*-hexane)

We have recently reported an analogous reaction to the above in which an equimolar ratio of Ag_2O and multidentate ligand (rather than a 1:2 ratio as above) was used to prepare a crystalline compound with the stoichiometry "$[Ag(hfa)(A{-}A)_{0.5}]_n$" (A−A = multidentate amine).[17] By using a similar methodology, the reaction for the preparation of compound **4** was repeated, but using only *1 molar equiv* of tetraglyme with respect to the silver(I) oxide, this time giving the crystalline compound $[Ag(hfa)(tetraglyme)_{0.5}]_n$ (**5**) (Scheme 2).

Scheme 2[a]

$$Ag_2O + 2H\text{-hfa} + \text{tetraglyme} \xrightarrow{(i), (ii), (iii)} 2[Ag(hfa)(tetraglyme)_{0.5}]_n\ (\mathbf{5}) + H_2O$$

[a] Legend: (i) thf/20 °C; (ii) filter, remove solvent; (iii) toluene/−20 °C

As mentioned above, the synthetic strategies adopted here are similar to those recently employed for the preparation of the amine-adducted hexafluoropentanedionatosilver(I) complexes [Ag(hfa)(A−A)] {(A−A) = multidentate amines[17]} and [Ag(hmten)][Ag(hfa)$_2$] (hmten = $Me_2N\{CH_2CH_2N(Me)\}_3Me$). However, during the syntheses for these compounds, the amine ligands were added to preformed "[Ag(hfa)]" (prepared from the reaction of Ag_2O and H-hfa in thf) in a toluene solution, rather than to the initial reaction mixture.[17] This avoided prereaction of the respective amines with acidic H-hfa ligands. For the glyme complexes, however, there was no significant difference in yields observed between the two synthetic methods.

Single crystals (fine needles) of compound **1** were obtained from a hexane/toluene solution (1:1 v/v) at −20 °C, which melted at ca. 5 °C to a viscous oil. Compounds **3**−**5** are reasonably air and moisture stable, while compound **1** is air sensitive, decomposing slowly over a few days in air to give a mixture of products and colorless crystals of the air stable compound $[Ag_2(hfa)(O_2CCF_3)(diglyme)_2]$ (**2**). Large blocks of compound **2** crystallized directly from the decomposition mixture and were obtained in a pure form by filtering the dark decomposition mixture [presumably removing finely suspended silver(I) oxide] over a few days and allowing the remaining mixture to crystallize.

All the compounds have good solubility in an extensive range of organic solvents, but especially in coordinating solvents such as ethers (e.g., thf and diethyl ether). Compounds **1**−**5** are likely to be soluble in supercritical carbon dioxide (scCO$_2$) at ca. 35 °C/2000 psi (theoretical density of ca. 0.80 g cm^{-3}) as a result of qualitative infusion tests into UHMWPE (ultrahigh molecular weight polyethylene) polymer disks.[18]

Spectroscopic Characterization and Physical Properties. The IR spectra in Nujol of compounds **1**−**5** show bands in the region 1670−1500 cm^{-1}, which are assigned as either ν(C=O) or ν(C=C) stretches of the hfa ligands.[15−17] For example, in the IR spectrum of complex **3**, the band at 1670 cm^{-1} is tentatively assigned to a ν(C=O) stretch, while the peaks at and 1533 and 1512 cm^{-1} are assigned as ν(C=C) stretching modes. Precise assignment of these different modes for all the complexes is not possible at present as vibrations are often coupled. Bands due to ν(C−O−C) for the coordinated glyme ligands occur at ca. 1245 and 1140 (broad) cm^{-1}, of which the latter band is shifted to higher frequency compared to the corresponding band for the unadducted glyme [*cf.* band at 1110 (broad) for diglyme, triglyme, and tetraglyme].[15,19]

Multinuclear (^{1}H and ^{13}C) NMR data are in agreement with the proposed molecular formulas. The ^{1}H NMR spectra for the complexes reveal a characteristic CH peak of the hfa ligand in the narrow range δ 5.71−5.83, suggesting only one environment for each β-diketonate ligand in solution (Table 1).

In all the ^{13}C NMR spectra two quartets (in the range δ 115.0−118.0 and ca. δ 176 ppm) are observed for the β-diketonate ligands (Table 2), due to the CF$_3$ carbons (of the hfa) and the adjacent carbonyl (CO) carbon, respectively. In the corresponding spectrum for **2**, two additional weak quartets are observed from the CF$_3$ carbon and the adjacent carboxylate (O$_2$C) carbon of the fluoroacetate ligand [centered at δ 129.1 ($^1J_{CF}$ = ca. 270 Hz) and δ 163.2 ($^2J_{CF}$ = 37 Hz), respectively]. All the spectra contain a single CH peak for the hfa ligand at ca. δ 86. The methylene (CH$_2$) signals of the polyether ligands are located in the narrow range δ 70.0−71.7 ppm. ^{19}F NMR analysis of complex **2** revealed two peaks at δ −77.3 and −73.7 (ratio of 2:1) due to the fluorines of hfa and carboxylate anions, respectively.

Compound [Ag(hfa)(diglyme)]$_2$ (**1**) melts at ca. 5 °C and exists as a viscous oil at room temperature, while its decomposition product **2** was observed to melt in the temperature range 65−68 °C. Similarly, the $[Ag(hfa)(triglyme)]_n$ (**3**) was observed to melt in the temperature range 64−66 °C. To show that $[Ag(hfa)(tetraglyme)_{0.5}]_n$ (**5**) exists as a discrete molecular species and not merely a 1:1 mixture of [Ag(hfa)(tetraglyme)] (**4**) and "$[Ag(hfa)]_n$", simultaneous thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were undertaken; plots for both compounds are shown in Figure 1.

[Ag(hfa)(tetraglyme)] (**4**) melts between ca. 46−49 °C in an open capillary, while a sharp endotherm at 44.6 °C (−18.0 mcal mg^{-1}) due to melting is observed in the DSC curve for this compound. The TGA plot for this compound appears to show a single stage weight loss in the range ca. 120−265 °C to give a final residue of 21.3% at 450 °C. However, the corresponding

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(17) (a) Blake, A. J.; Darr, J. A.; Li, W.-S.; Poliakoff, M. *J. Chem Soc., Dalton Trans.* **1997**, 2869 and references therein. (b) Multidentate amines (A−A) = $Me_2NCH_2CH_2NHMe$ (trimen), $Me_2N\{CH_2CH_2N(Me)\}_2Me$ (pmdien), and $Me_2N\{CH_2CH_2N(Me)\}_3Me$ (hmten)}.

(18) Webb, P.; Howdle, S., unpublished results (1998). In initial experiments, the complexes were impregnated into UHMWPE disks using supercritical carbon dioxide as the solvent. Exposure of the impregnated disks to strong sunlight (3 h) resulted in visible darkening of the polymers. The polymer materials were then treated to a dynamic flow of supercritical carbon dioxide (10 min) in the hope of removing any residual organic ligands/complexes formed from the visible decomposition of the initial silver complexes. TEM analyses of thin microtomed sections of these composite materials revealed dark nanometer-sized particles [likely to be silver(I) oxide formed from the reaction of the complexes and water]. Studies are currently in progress to identify the exact composition of these particles (i.e. silver metal or silver oxide) and to further characterize the inorganic and organic decomposition products of the complexes.

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Table 1. ^{1}H NMR Chemical Shifts (δ) for Complexes **1**−**5** [CDCl$_3$][a]

compound	CH$_3$	CH$_2$	CH$_2$	CH$_2$	CH
1	3.31 (s, 12H)	3.50 (m, 8H)	3.57 (m, 8H)	−	5.71(s, 2H)
2	3.42 (s, 12H)	3.61 (m, 8H)	3.68 (m, 8H)	−	5.87 (s, 1H)
3	3.35 (s, 6H)	3.57 (m, 4H)	3.67 (m, 4H)	3.70 (m, 4H)	5.78 (s, 1H)
4	3.56 (s, 6H)	3.55 (m, 4H)	3.63 (m, 4H)	3.69 (s, 8H)	5.76 (s, 1H)
5	3.41 (s, 6H)	3.59 (m, 4H)	3.67 (m, 4H)	3.74 (d, 8H),	5.83 (s, 2H)

[a] Key: s = singlet, d = doublet, m = multiplet.

Table 2. ^{13}C NMR Chemical Shifts (δ) for Complexes **1**−**5** [CDCl$_3$][a]

compound	CH$_3$	CH$_2$	CH$_2$	CH$_2$	CH	CF$_3$	CO
1	59.7	70.2	−	71.4	85.3	118.0 (q)	176.0 (q)
2	60.3	70.3	−	71.5	86.5	117.4 (q)†	176.0 (q)†
3	59.6	70.3	70.7	71.6	86.0	115.0 (q)	176.6 (q)
4	59.5	70.2	70.3	71.7	85.6	117.0 (q)	176.5 (q)
5	60.2	70.0	70.3	71.6	85.3	117.7 (q)	176.6 (q)

[a] Keys: "†", also quartets (q) at δ 129.13 and 163.2 due to CF$_3$ and CO, respectively, of acetate ligand; all peaks are singlets unless stated otherwise.

Table 3. Assignments for Selected Molecular Ions Observed in the Mass Spectra for Complexes **1**−**5**[a]

	m/z^+				
	1	**2**	**3**	**4**	**5**
[Ag(tetraglyme)]$^+$	329	−	329	329	−
[Ag(triglyme)]$^+$	285	−	285	−	−
[Ag(diglyme)]$^+$	241	241	−	−	−
[Ag(hfa) − 2CF$_3$]$^+$	−	−	199	−	199
[CH$_3$O(CH$_2$CH$_2$O)$_2$CH$_2$]$^+$	−	−	133	−	133
[Ag]$^+$	107	107	107	107	107

[a] Fast atom bombardment; positive ion (FAB$^+$), selected ions.

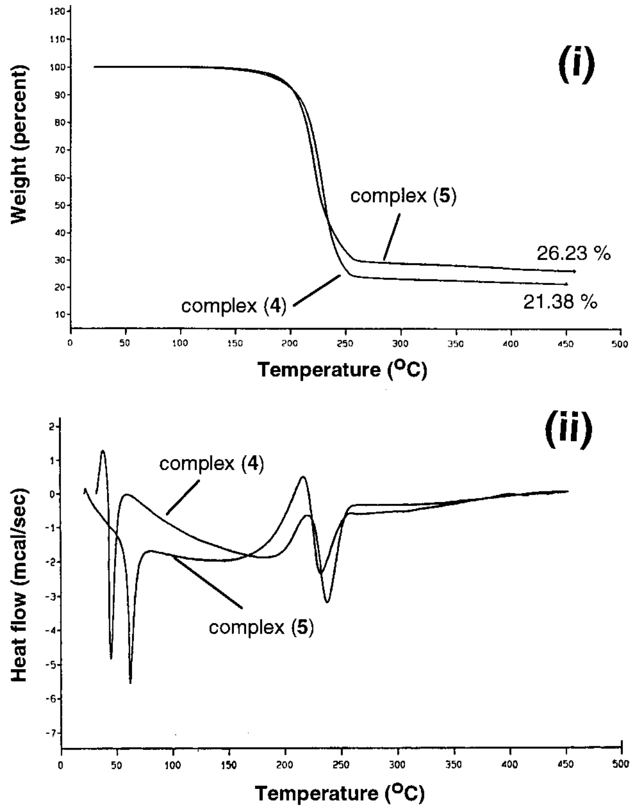

Figure 1. (i) Thermogravimetric analysis (TGA) and (ii) differential scanning calorimetry (DSC) plots for [Ag(hfa)(tetraglyme)] (**4**) and [Ag(hfa)(tetraglyme)$_{0.5}$]$_n$ (**5**).

DSC plot shows at least two broad overlapping isotherms in this temperature range (an exotherm and an endotherm centered at ca. 222 and 231 °C, respectively). In contrast to compound **4**, [Ag(hfa)(tetraglyme)$_{0.5}$]$_n$ (**5**) melts between ca. 59−62 °C in an open capillary, while a sharp endotherm at 62.0 °C (−10.4 mcal mg^{-1}) due to melting was observed in the DSC curve for this compound. The TGA plot for this compound is similar to that for compound **4** [Figure 1, (i)], but a higher proportion of residue is obtained at 450 °C (26.2% compared to 21.3%). As in the DSC plot for **4**, that for compound **5** shows at least two overlapping isotherms in this temperature range in this case are centered at ca. 217 and 235 °C, respectively [Figure 1, (ii)].

The above TGA/DSC data suggest that the compounds melt at significantly different temperatures, but undergo similar decomposition reactions when heated above 120 °C in this manner. The weight percentages for both residues obtained at 450 °C are very close to the values expected for silver(I) oxide; for compounds **4** and **5**, silver(I) oxide would be expected to give residues of 21.4 and 27.1%, respectively (observed 21.4 and 26.2%, respectively). However, visual inspection of the residues suggested that metallic silver was formed, along with some black, possibly carbonaceous material.

Our attempts to sublime complexes **1**−**5** at reduced pressures of 1 × 10^{-2} Torr in the temperature range 130−150 °C resulted rather in decomposition of the compounds to give black residues in the sublimation vessel. This was not surprising given the relatively poor match between the O-donor ligand and the silver(I) cation: these complexes would therefore be unsuitable as CVD precursors to silver or silver oxide thin films.

The mass spectral data obtained in the FAB$^+$ (fast atom bombardment positive ion) mode revealed that the respective [Ag(L−L)]$^+$ (where L−L = glyme) molecular ions are observed (Table 3). Some fragmentation or recombination of the glyme ligands may also be occurring under these conditions for [Ag(hfa)(diglyme)]$_2$ (**1**), as molecular ion peaks corresponding to the chain expanded adducts [Ag(tetraglyme)]$^+$ and [Ag(triglyme)]$^+$ were also observed.

Molecular Structures. Single-crystal X-ray diffraction studies of complexes **1**, **2**, and **4** were undertaken to identify unambiguously the structures and natures of the bonding in the compounds.

[Ag(hfa)(diglyme)]$_2$ (1). A crystal structure determination of compound **1** established that it is dimeric as shown in Figure 2. The structure contains two silver atoms which are bridged by four oxygens from two hfa ligands; each silver atom is also coordinated by a chelating diglyme molecule. The dimeric structure has some similarities with the recently reported compound [Ag$_2$(hfa)$_2$(dmcod)$_2$] (dmcod = 1,5-dimethylcyclooctadiene), in which the hfa ligands display what could be described as a μ_4:η^2-coordination.[20] The two silver atoms are related by a crystallographic two-fold which bisects the Ag$\cdots$Ag vector; for Ag1, one Ag−O(hfa) bond (Ag1−O1A) is significantly shorter at 2.528(4) Å, while three Ag−O(hfa) bonds (Ag1−O1, Ag1−O2, Ag1−O2A) are significantly longer at 2.593(4), 2.609(4), and 2.621(4) Å, respectively. Although the

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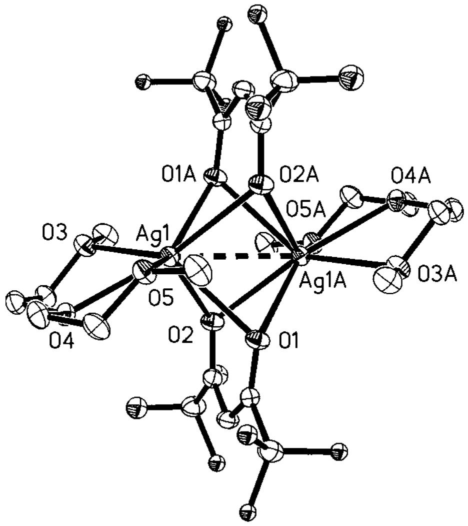

Figure 2. Structure of [Ag(hfa)(diglyme)]$_2$ (**1**), showing the atom numbering scheme (50% probability for the thermal ellipsoids). Hydrogen atoms are omitted for clarity. Selected bond length Ag1$\cdots$Ag1A = 2.9226(10) Å.

nature of these three long Ag−O(hfa) bonds is unclear, we would suggest they are weak bonding interactions. Surprisingly, the shortest and longest Ag−O contacts in the present compound are observed for the polyether ligand: the Ag−O bond distances are 2.657(4), 2.486(4), and 2.579(4) Å for O3, O4, and O5, respectively (Ag1−O3 is considered as another weak bonding interaction).

The preference for a dimeric (seven coordinate) rather than a monomeric (five coordinate silver) structure as observed for the three nitrogen-donor analogue [Ag(hfa)(pmdien)][17] may be as a result of a poorer metal to neutral ligand match in the case of compound **1**, which requires additional coordination of oxygens (via oligomerization) to stabilize the silver cations. The Ag$\cdots$Ag distance in this compound is 2.9226(10) Å, which is slightly less than the corresponding distance observed in [Ag$_2$(dppm)$_2$(NO$_3$)$_2$] [3.085(1) Å],[21] [Ag$_2$(hfa)$_2$(cod)$_2$] [2.955(2) Å],[22] [Ag$_2$(hfa)$_2$(dmpm)$_2$] [3.153(1) Å],[23] [Ag$_2$(hfa)$_2$(dmcod)$_2$] [3.0134(3) Å],[20] and [Ag$_4$(hfa)$_4$(SEt$_2$)] [3.046(2) Å],[24] and in all these cases the Ag$\cdots$Ag distances have been assigned as nonbonding interactions.

[Ag$_2$(hfa)(O$_2$CCF$_3$)(diglyme)$_2$] (2). The X-ray crystal structure of compound **2** contains two Ag(I) ions which are bridged by four oxygens from both hfa and fluoroacetate ligands; each cation is also coordinated to a chelating diglyme molecule (Figure 3). The two silver cations in **2** are related by a plane of symmetry which bisects the Ag−Ag vector. The Ag$\cdots$Ag distance is 2.9513(6) Å, slightly longer than the corresponding distance observed in **1**.

Surprisingly, all six Ag−O contacts possible for the neutral polyether ligands in **2** are observed within a narrow range of 2.545(3)−2.496(3) Å [average 2.523 Å]. For the anionic hfa ligand, three of the four Ag−O(hfa) distances are of similar length at 2.468(3), 2.534(3), and 2.537(3) Å, while the fourth [Ag1−O6] is significantly longer at 2.620(3) Å. The nature of this fourth Ag−O(hfa) bond is unclear, but we suggest it is a weak bonding contact and consequently the hfa ligand could be described as displaying a μ_4:η^2-bridging mode as observed in **1**. By far the shortest Ag−O distances, 2.304(3) and 2.266(3) Å for Ag1−O4 and Ag2−O5, respectively, involve the fluoroacetate ligand and are indicative of strong bonding interactions.

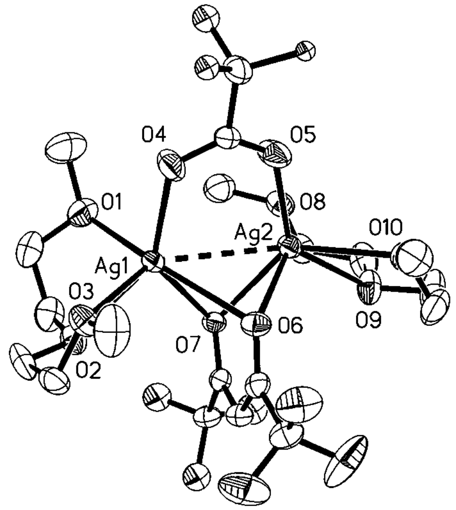

Figure 3. Structure of [Ag$_2$(hfa)(O$_2$CCF$_3$)(diglyme)$_2$] (**2**), showing the atom numbering scheme (50% probability for the thermal ellipsoids). Hydrogen atoms are omitted for clarity. Selected bond length Ag1$\cdots$Ag2 = 2.9513(6) Å.

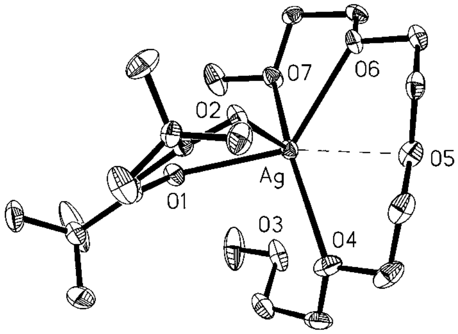

Figure 4. Structure of [Ag(hfa)(tetraglyme)] (**4**), showing the atom numbering scheme (30% probability for the thermal ellipsoids). Hydrogen atoms are omitted for clarity. Selected interatomic distance Ag$\cdots$O3 = 2.949(3) Å.

[Ag(hfa)(tetraglyme)] (4). An X-ray structure determination of compound **4** showed that as expected it is monomeric. The stoichiometry thus determined is in good agreement with the spectroscopic data. The compound (shown in Figure 4) contains an Ag(hfa) moiety coordinated to a tetraglyme ligand in which four of the five polyether oxygens are located within bonding distance [range of 2.543(3)−2.742(3) Å] of the silver cation [the bond at 2.742(3) Å is assigned as a very weak contact, possibly a nonbonding interaction (shown as a dashed line in Figures 4 and 5)]. The fifth polyether oxygen [O3] is located 2.949(3) Å from the Ag cation, which is well in excess of the separation expected for a viable Ag−O bond. Furthermore, a side view (Figure 5; line diagram with circles representing oxygens) of complex **3** as viewed in the approximate meridional plane of the four coordinating polyether oxygens [O4, O5, O6, and O7], shows that the uncoordinated terminal polyether oxygen O3, is clearly out of this plane and bends away from the direction of the silver cation. The overall geometry of the silver coordination sphere does not conform to any ideal shape but could be described as a severely distorted pentagonal bipyramid with O1 and O5 occupying the axial positions and

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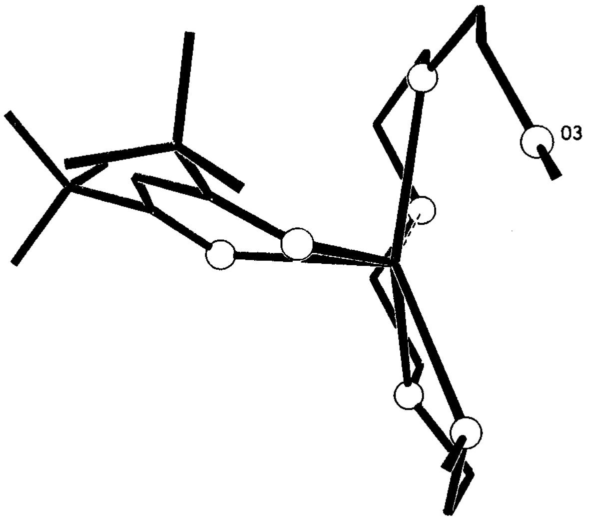

Figure 5. Ball (oxygen) and stick representation of the structure of compound **4** as viewed parallel to the approximate meridional plane of the four coordinating polyether oxygens [O(4), O(5), O(6), and O(7)], showing the uncoordinated terminal polyether oxygen O(3) bending out of this plane.

O2, O3, O4, O6, and O7 forming an approximate equatorial plane. The O−Ag−O angle for the two trans-coordinated glyme oxygens is 149.73(9)°.

The Ag−O(hfa) bond lengths [2.416(3) and 2.441(3) Å] are similar and can be compared to the range 2.282−2.642 Å for other silver(I) complexes involving purely chelating hfa ligands and the ranges 2.419(4)−2.376(4) and 2.292(6)−2.327(6) Å for the recently reported multidentate amine-adducted complexes [Ag(hfa)(pmdien)] and [Ag(hmten)][Ag(hfa)$_2$], respectively.[17,23−25] These bonds are significantly shorter (by ca. 0.2 Å) than those observed for the bridging μ_4:η^2-hfa ligands in compound **1**. The structure of this compound can be compared to those of the heavier alkali metal β-diketonate compounds incorporating multidentate glymes and crown ethers, which are generally polymeric.[26] This is undoubtedly due to the relatively less coordinatively demanding nature of the silver cation in comparison to alkali metal cations.

Concluding Remarks

Although this research has not yielded compounds with suitably high volatilities for CVD precursors, we have demonstrated the formation of discrete molecular species which are well defined and obtained in excellent yields. Our endeavors have shown that, by careful choice of the multidentate ligand, in selected cases we have been able to improve the air and moisture stability of hexafluoropentanedionatosilver(I). Coordination of a polyether ligand(s) $CH_3O(CH_2CH_2O)_mCH_3$ (m = 3 or 4) to the "[Ag(hfa)]" moiety is an inexpensive and effective method of ensuring that the products have good "shelf life" and solubility in a range of solvents including supercritical carbon dioxide (scCO$_2$).

Our recent observations that monomeric silver(I) β-diketonate complexes with a wide range of coordination numbers can be stabilized are in stark contrast to the chemistry of the corresponding alkali metal analogues which generally have been observed to give polymeric complexes. This is likely to be due to the less demanding coordination requirements of silver ions compared to the alkali metal ions. This would explain the observation of a partially coordinated tetraglyme molecule in the structure of [Ag(hfa){$CH_3O(CH_2CH_2O)_4CH_3$}]. It could be envisaged that this complex may be a useful precursor to heterometallic species by utilizing the uncoordinated terminal polyether oxygen to bridge to an unsaturated Lewis acid metal complex.

Experimental Section

General Procedures and Starting Materials. All reactants and products were manipulated under a nitrogen atmosphere (Schlenk line), argon atmosphere (glovebox) or in vacuo, with exclusion of moisture and air. The solvents were predried and then distilled prior to use and were stored over 4 Å molecular sieves under an atmosphere of nitrogen in a glass storage vessel fitted with a Young's high-vacuum PTFE stopcock. Qualitative solubility/impregnation tests were performed by using supercritical carbon dioxide (40−50 °C/ca. 2500 psi) to infuse the compounds into thin disks of ultrahigh molecular weight polyethylene.[18] Tests were conducted in a sealed Thar Designs high-pressure extraction vessel (10 cm^3 volume, rated to 10 000 psi/100 °C) using gaseous carbon dioxide (grade 3.5 purity, Cryoservices Ltd) without further purification. Silver(I) oxide (Aldrich) was used as purchased. Tetraglyme, triglyme, and 1,1,1,5,5,5-hexafluoropentane-2,4-dione (H-hfa) were stored over 4 Å molecular sieves prior to use, while diglyme (anhydrous) was used as obtained (Aldrich).

Instrumentation. IR spectra were recorded on a Nicolet 5DX FT-IR interferometer as Nujol mulls between KBr plates, in the region 4000−400 cm^{-1}. All NMR solution spectra were recorded on a Bruker Avance DPX 300 MHz NMR spectrometer: ^{1}H NMR spectra were recorded at 300.13 MHz (at 25 °C), while ^{13}C{^{1}H} NMR solution spectra were obtained at 73.03 MHz. Chemical shifts were referenced using the *protio* impurities of the deuterated solvent. Elemental analyses were performed at Nottingham by the School of Chemistry microanalytical service. Mass spectrometry data were obtained on a VG Autospec instrument (Nottingham) in the FAB (positive ion) mode. Controlled thermogravimetric analysis (TGA) and differential scanning calorimetric (DSC) measurements of the complexes were done using a Polymer Laboratories 1500H simultaneous thermal analyzer, controlled by a Omni Pro 486DX-33 PC. The weight of the samples investigated was between 19 and 27 mg. The measurements were carried out in alumina crucibles under an atmosphere of flowing (30 cm^3 min^{-1}) nitrogen gas, using heating rates of 10 °C min^{-1}. Melting points were recorded in unsealed capillaries and are uncorrected.

[Ag(hfa)(diglyme)]$_2$ (1). Silver(I) oxide (2.24 g, 9.6 mmol) was weighed into a Schlenk tube and suspended in thf (40.0 cm^3) and diglyme (2.57 g, 19.2 mmol). To this mixture was added H-hfa (2.70 cm^3, 19.2 mmol), with rapid stirring and the reaction left to stir for 30 min. Almost all of the black solid dissolved during this time. The mixture was filtered on a very fine sinter packed with Celite and glass wool. The solvent was removed in vacuo to give a yellow oil. The oil was layered with *n*-hexane (30 cm^3) and left to stand at −20 °C for 2 h, after which time a crop of colorless needles was obtained. The crystals were filtered while still cold on a Büchner funnel and quickly transferred into a vial. After a few seconds at room temperature they melt to a yellow oil again. The oil was held under reduced pressure again for 1 h (yield 5.4 g, 63%, mp ca. 5 °C. Found for $C_{11}H_{15}O_5AgF_6$: C, 29.21; H, 3.52. Calcd: C, 29.46; H, 3.35%. υ_{max}/cm^{-1} (Nujol): 1663 s, 1533 s, 1450 m, 1245 s, 1183 s, 1135 s, 1012 m, 930 w, 855 m, 834 w, 786 m, 738 w, 656 m, 567 m, 519 vw.

[Ag$_2$(hfa)(O$_2$CCF$_3$)(diglyme)$_2$] (2). [Ag(hfa)(diglyme)]$_n$ (1.5 g, 3.34 mmol) was left on a watchglass in a well-ventilated fume cupboard and left to decompose for 48 h. The resulting oil was filtered on a Büchner funnel and then placed on a watchglass for a further 48h. Small colorless blocks crystallized from the oil (0.94 g, 35%), mp 65−68 °C. Anal. Calcd for $C_{19}H_{29}O_{10}Ag_2F_9$: C, 28.42; H, 3.61. Found: C, 27.87; H, 3.58. IR (Nujol): 1699 m, 1675 s, 1551 s, 1533 s, 1260 s, 1185 broad, s, 1128 s, 1089 m, 660 w cm^{-1}. ^{19}F NMR (CDCl$_3$): δ −77.3 (s, CF$_3$ hfa), −73.7 (s, CF$_3$ of O$_2$CCF$_3$).

[Ag(hfa)(triglyme)] (3). Silver(I) oxide (2.24 g, 9.6 mmol) was weighed into a Schlenk tube and suspended in thf (40 cm^3) and triglyme

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Table 4. Crystal Data and Details of Data Collection for $[Ag_2(hfa)_2(diglyme)_2]$ (**1**), $[Ag_2(hfa)(O_2CCF_3)(diglyme)_2]$ (**2**), and [Ag(hfa)(tetraglyme)] (**4**)

	1	**2**	**4**
formula	$C_{22}H_{28}Ag_2F_{12}O_{10}$	$C_{19}H_{29}O_{10}Ag_2F_9$	$C_{15}H_{23}AgF_6O_7$
fw	896.18	803.15	537.20
space group	$C2/c$	$P\bar{1}$	$P2_1/c$
a, Å	21.376(3)	9.0945(12)	14.152(3)
b, Å	8.4143(17)	9.4110(13)	16.996(3)
c, Å	21.067(3)	17.803(2)	8.620(2)
α, deg	90	96.109(14)	90
β, deg	124.05(1)	101.649(13)	106.99(2)
γ, deg	90	105.06(2)	90
vol, Å^3	3139.5(9)	1420.6(3)	1982.9(7)
Z	4	2	4
ρ_{calcd}, g/cm^3	1.896	1.878	1.800
μ, mm^{-1}	1.368	1.485	1.106
λ, Å	0.710 73	0.710 73	0.710 73
T, K	150	150	150
R_1,[a] wR_2[b]	0.0448, 0.1177	0.0344, 0.0855	0.0370, 0.0773

[a] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$.

(3.41 g, 19.2 mmol). To this mixture was added H-hfa (2.70 cm^3, 19.2 mmol), with rapid stirring and the reaction left to stir for 30 min. Most of the black solid dissolved during this time to yield a slightly turbid solution. The mixture was filtered on a fine sinter packed with Celite and glass wool. The solvent was removed in vacuo to give white solid. The solid was redissolved in cold toluene (15 cm^3), layered with *n*-hexane (10 cm^3) and left to stand overnight. The next day the solution was placed at −20 °C and over a period of 3 h yielded a crop of colorless crystals which were filtered on a Büchner funnel (yield 6.9 g, 73%), mp 64−66 °C; decomposes >161 °C. Found for $C_{13}H_{19}O_6AgF_6$: C, 30.93; H, 3.89. Calcd: C, 31.70; H, 3.86. υ_{max}/cm^{-1} (Nujol): 1670 m, 1533 m, 1512 m, 1245 m, 1183 m, 1135 m, 1012 w, 937 w, 841 vw, 779 w, 731 w, 656 vw, 574 w.

[Ag(hfa)(tetraglyme)] (4). This compound was prepared using a method similar to that employed for compound **2**, but using tetraglyme (4.26 g, 19.2 mmol) instead of triglyme. The solution was placed at −20 °C and over a period of 3 h yielded a large crop of colorless block crystals which were filtered on a Büchner funnel (yield 7.7 g, 75%), mp 46−49 °C; decomposes >176 °C, (Found: C, 33.48; H, 4.51%. $C_{15}H_{23}O_7AgF_6$ requires C, 33.58; H, 4.29%); υ_{max}/cm^{-1} (Nujol) 1663 w, 1519 m, 1245 s, 1142 s, 1087 s, 1019 s, 937 m, 841 w, 779 w, 745 w, 656 w, 574 w.

$[Ag(hfa)(tetraglyme)_{0.5}]_n$ (5). This compound was prepared using a method similar to that employed for compound **3**, but using only one molar equivalent of tetraglyme (2.13 g, 9.6 mmol) with respect to silver(I) oxide. The solution was placed at −20 °C and over a period of 3 h yielded a small crop of colorless needles which were filtered on a Büchner funnel (yield 4.2 g, 52%), mp 59−62 °C; decomposes >164 °C. Found for $C_{10}H_{12}O_{4.5}AgF_6$: C, 28.18; H, 2.82. Calcd: C, 28.23; H, 2.82. υ_{max}/cm^{-1} (Nujol): 1663 m, 1526 m, 1245 s, 1183 s, 1142 s, 1012 m, 937 m, 834 m, 779 m, 738 w, 656 w, 567 w, 519 w.

Crystal Structure Determinations. Crystals of **1**, **2**, and **4** were mounted on a two-stage glass fiber with RS3000 perfluoropolyether oil (Hoechst) before being transferred to the diffractometer. The data were collected using a Stoe Stadi-4 four-circle diffractometer equipped with Oxford Cryosysytems open-flow cryostat.[27] The data were corrected for Lorentz and polarization effects, and absorption corrections based on ψ scans were applied.

Table 5. Selected Bond Lengths (Å) and Angles (deg) for **1**

Ag1−O1	2.593(4)
Ag1−O2	2.609(4)
Ag1−O3	2.657(4)
Ag1−O4	2.486(4)
Ag1−O5	2.579(4)
Ag1−O1A	2.528(4)
Ag1−O2A	2.621(4)
O1−Ag1−O2	65.70(12)
O3−Ag1−O4	65.59(13)
O4−Ag1−O5	66.46(13)
Ag1−O1−Ag1A	69.6(1)
Ag1−O2−Ag1A	67.9(1)

Table 6. Selected Bond Lengths (Å) and Angles (deg) for **2**

Ag1−O1	2.509(4)	Ag2−O8	2.531(3)
Ag1−O2	2.532(3)	Ag2−O9	2.529(3)
Ag1−O3	2.496(3)	Ag2−O10	2.545 (3)
Ag1−O4	2.304(3)	Ag2−O5	2.266(3)
Ag1−O6	2.620(3)	Ag2−O6	2.534(3)
Ag1−O7	2.537(3)	Ag2−O7	2.468(3)
O1−Ag1−O2	68.27(11)	O8−Ag2−O9	66.88(11)
O2−Ag1−O3	66.94(10)	O9−Ag1−10	65.80 (10)

Table 7. Selected Bond Lengths (Å) and Angles (deg) for **4**

Ag1−O1	2.416(3)
Ag1−O2	2.441(3)
Ag1−O4	2.570(3)
Ag1−O5	2.742(3)
Ag1−O6	2.543(3)
Ag1−O7	2.543(3)
O1−Ag−O2	74.83(10)
O3−Ag−O4	61.49(10)
O4−Ag−O5	63.10(10)
O5−Ag−O6	63.83(10)
O6−Ag−O7	66.01(10)

Details of crystal data and structure analysis are given in Table 4. The structures were solved by direct methods[28] and were refined by full-matrix least squares on F^2.[29] Anisotropic displacement parameters were allowed for all ordered non-hydrogen atoms. Hydrogen atoms were initially placed in geometrically calculated positions and thereafter allowed to ride on their parent C atoms with $U_{iso}(H) = 1.2U_{eq}(C)$. For compound **1**, rotational disorder of the CF_3 groups was observed and each F atom was resolved into three equal components. For **2**, two of the CF_3 groups were found to be disordered. Each F atom was resolved into two equally populated components in one CF_3 group while the second disordered CF_3 group was resolved into three equally populated orientations. Details of the structure determinations are given in Table 4, while selected bond lengths and angles for these compounds are given in Tables 5, 6, and 7. Illustrations were generated using SHELXTL/PC,[30] and molecular geometry calculations utilized SHELXTL/PC,[30] SHELXL-96, and SHELXL-97.[29]

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Supporting Information Available: X-ray crystallographic files, in CIF format, for the structure determinations of **1**, **2**, and **4** are available on the Internet only. Access information is given on any current masthead page.

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