Synthesis and Characterization of Lewis-base Adducts of 1,1,1,5,5,5-Hexafluoroacetylacetonatosilver(I)†

Chongying Xu,[a] Thomas S. Corbitt,[a] Mark J. Hampden-Smith,*[a] Toivo T. Kodas*[b] and Eileen N. Duesler[a]
[a] *Department of Chemistry, University of New Mexico, Albuquerque, NM 87131, USA*
[b] *Department of Chemical Engineering, University of New Mexico, Albuquerque, NM 87131, USA*

The compounds $[\{Ag(hfacac)\}_mL_n]$ [hfacac = 1,1,1,5,5,5-hexafluoroacetylacetonate, L = norbornadiene (nbd), $m = 2$, $n = 1$; L = SMe_2, SEt_2, $SPr^n{}_2$ or $SBu^n{}_2$, $m = 1$, $n = 1$; L = 1,4-oxathiane, $m = 1$, $n = 1$ or 2] were prepared by the reaction between the Lewis bases, L, Hhfacac and Ag_2O in the appropriate ratios. In addition, the intermediate $[\{Ag(hfacac)\}_2(H_2O)]$, formed by the reaction of Ag_2O with 2 equivalents of Hhfacac in the absence of L was isolated. These species were characterized by ^1H and ^{13}C NMR and Fourier-transform IR spectroscopy and by combustion elemental analysis. Three examples were structurally characterized by single-crystal X-ray diffraction. The compound $[\{Ag(hfacac)\}_2(H_2O)]$ is oligomeric by virtue of intermolecular hydrogen bonding between the co-ordinated water molecule and the oxygen atoms in the hfacac ligand in an adjacent molecule. In addition there is a bonding interaction between the methine carbon in the hfacac ring of one molecule and the silver centre in an adjacent molecule. The compound $[\{Ag(hfacac)\}_2(nbd)]$ is dimeric leading to a tetranuclear molecular unit in which the hfacac ligands both chelate and bridge, with unidentate nbd ligands. The compound $[Ag(hfacac)(C_4H_8OS)_2]$ is monomeric in the solid state with the 1,4-oxathiane ligands co-ordinated to the silver(I) centre exclusively *via* the S atoms. The silver has a severely distorted tetrahedral geometry with an enlarged S–Ag–S angle [149.6(1)°] and a reduced O–Ag–O angle [74.4(2)°] which is characteristic of (β-diketonato)bis(ligand)metal compounds where M = Ag or Cu.

The synthesis of compounds containing the coinage metals, Cu, Ag and Au, is attracting interest as a result of the potential technological applications of films of these metals formed by chemical vapour deposition (CVD).[1–5] Copper, silver and gold films can be used as contacts in microelectronic devices[3–5] and silver films are being used in ceramic superconductors[3] and membrane separations.[6–8] The design criteria for compounds containing these metals are that they be volatile, thermally stable at room temperature and deposit pure metal films at high rates and at relatively low temperatures.[9] There are now a variety of copper-(I)[4,10–17] and -(II)[18–21] and gold-(I)[22] and -(III)[23,24] compounds which, to a large degree, fulfil these criteria. However, there is a distinct paucity of silver compounds suitable for CVD. The major problem with silver(I) species is that they are generally either thermally unstable or involatile and frequently both. Of the species that have been studied, including $[\{Ag[C(CF_3)=CF(CF_3)]\}_4]$,[25] $[Ag(\eta^5\text{-}C_5H_5)(PR_3)]$ (R = *e.g.*, Me),[26,27] $[Ag(O_2CCF_3)]_n$,[28] and $[Ag(hfacac)(PMe_3)_n]$[29,30] ($n = 1$ or 2; hfacac = 1,1,1,5,5,5-hexafluoroacetylacetonate), $[Ag(hfacac)(PMe_3)]$[29] is most suitable for CVD of silver films. It might be expected that $[Ag^I(hfacac)L]$ compounds similar to the $[Cu^I(hfacac)L]$ which have been studied extensively for CVD of Cu[4,14,15,31–37] might be suitable for CVD of Ag. However, the silver(I) analogues appear qualitatively less volatile. The origin of this involatility has been attributed previously to the larger ionic radius of Ag^I compared to that of Cu^I.[38] This can result in a higher degree of aggregation for the silver(I) derivative in a pair of compounds with otherwise identical empirical formulae as was recently demonstrated for the case of $[\{M(hfacac)(cod)\}_n]$ (cod = cycloocta-1,5-diene) where for M = Cu^I, $n = 1$, but for M = Ag^I, $n = 2$.[38] While low volatility can be alleviated to some extent by utilizing non-conventional precursor delivery methods,[39] it is valuable to derive a better understanding of factors that affect oligomerization in these silver(I) species.

In this work we sought to synthesise and characterize a number of new silver(I) compounds with the empirical formula $[\{Ag(hfacac)\}_mL_n]$ to derive a better understanding of the structural variation in these compounds. In particular, the degree of oligomerization, the co-ordination geometry and number of Ag^I and the co-ordination mode of the hfacac ligand are relevant to studies of reactions of $[Cu^I(hfacac)L]$ compounds.[40,41] Although a number of silver(I) complexes of this type have been prepared,[42] relatively few have been structurally characterized. In addition, we also wished to isolate and identify the species described as '$[Ag^I(hfacac)]$' in the literature[42] which has been used as a reactive intermediate to prepare $[\{Ag(hfacac)\}_mL_n]$ compounds. The analogous copper(I) compound cannot be isolated, even at low temperatures in solution, because it is unstable with respect to disproportionation to give copper metal and $[Cu(hfacac)_2]$; this reaction is also the basis of the CVD of Cu from $[Cu^I(hfacac)L]$ compounds.[4] Furthermore, it is likely that '$[Ag^I(hfacac)]$' is oligomeric and therefore reaction with Lewis bases might be predisposed to form oligomeric products.

Experimental

All manipulations were carried out under an atmosphere of dry dinitrogen using standard Schlenk techniques. All hydrocarbon and ether solvents were dried and distilled from sodium–benzophenone and stored over 4 Å molecular sieves. Silver(I) oxide, 1,1,1,5,5,5-hexafluoroacetylacetone, and alkyl sulfides were obtained from Aldrich Chemical Co. and used without further purification. The reagent bicyclo[2.2.1]hepta-2,5-diene (norborna-2,5-diene, nbd) was obtained from Eastman Kodak

---

† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.

Company and used without further purification. Elemental analyses were performed by Ms. R. Ju at the Department of Chemistry, University of New Mexico. Nuclear magnetic resonance spectra were recorded on a Bruker AC-250P spectrometer by using the protio impurities of the deuteriated solvents as reference for ^1H and the ^{13}C resonance of the solvents as reference for $^{13}C-\{^1H\}$. Infrared spectra were recorded on a Perkin-Elmer model 1620 FTIR spectrophotometer. X-Ray powder diffraction data were collected on a Siemens D5000 diffractometer and melting-point data were measured on a Thomas-Hoover capillary apparatus.

Syntheses.—Similar procedures were employed to prepare all the compounds described.

$[\{Ag(hfacac)\}_2(H_2O)]$. Silver(I) oxide (1.40 g, 6.04 mmol) was placed in a Schlenk flask (100 cm^3), wrapped with aluminium foil and diethyl ether (40 cm^3) was added. The flask was cooled to −20 °C and an aliquot of Hhfacac (2.60 g, 12.50 mmol, 1.03 equivalents) was injected into the rapidly stirred solution. The entire solution was stirred for 3 h at −20 °C, then filtered to remove any remaining solid. Removal of volatile components *in vacuo* gave 3.56 g white powder, a yield of 90.4% for the crude product. A solution of the above product (1.0 g) in methylene chloride (≈ 30 cm^3) was cooled at 0 °C to give colourless crystals, 0.80 g (80% yield). M.p. ≈100 °C (decomp.). IR (KBr disc): 3506w, 1654s, 1531m, 1514w, 1469m, 1320w, 1261s, 1258s, 1203s, 1146s, 802m, 663m, 580m and 524w cm^{-1}. NMR (CD_2Cl_2): ^1H, δ 5.32 (s, 2 H, CH of hfacac) and 1.79 (br, 2 H, OH of H_2O); $^{13}C-\{^1H\}$, δ 177.2 (q, *J* 32.1, C=O of hfacac), 118.6 (q, *J* 290.6 Hz, CF_3 of hfacac) and 87.4 (s, CH of hfacac) (Found: C, 18.45; H, 0.20. Calc. for $C_{10}H_4Ag_2F_{12}O_5$: C, 18.55; H, 0.50%).

$[Ag(hfacac)(SEt_2)]$. *Method A*. Silver(I) oxide (2.80 g, 12.08 mmol) was placed in a Schlenk flask (100 cm^3) and dry diethyl ether, (*ca.* 50 cm^3) was added. The whole flask was wrapped with aluminium foil. The slurry was stirred at −20 °C and Hhfacac (5.54 g, 26.63 mmol, 1.10 equivalents) was added by syringe. After 15 min, SEt_2 (2.53 g, 28.07 mmol, 1.16 equivalents) was added by syringe. The reaction mixture was stirred overnight at −20 °C. Then the solution was warmed to room temperature and filtered to remove any insoluble components. The volatile components were removed *in vacuo* to give 8.84 g (90% yield) of low-melting crystalline needles. The product could also be recrystallized from pentane at −30 °C to give colourless needles. M.p. 54–55 °C. IR (KBr disc): 2984w, 2938w, 1667s, 1522s, 1377w, 1314w, 1257s, 1203s, 1144s, 793m, 662m and 578m cm^{-1}. NMR (C_6D_6): ^1H, δ 6.28 (s, 1 H, CH of hfacac), 1.74 (q, 4 H, *J* 7.3, SCH_2 of SEt_2), and 0.68 (t, 6 H, *J* 7.3, CH_3 of SEt_2); $^{13}C-\{^1H\}$, δ 177.5 (q, *J* 32.1 Hz, C=O of hfacac), 87.3 (s, CH of hfacac), 28.1 (s, SCH_2 of SEt_2) and 14.5 (s, CH_3 of SEt_2) (Found: C, 26.90; H, 3.00. Calc. for $C_9H_{11}AgF_6O_2S$: C, 26.70; H, 2.75%).

Method B. A Schlenk flask (50 cm^3) was charged with $[\{Ag(hfacac)\}_2(H_2O)]$ (0.350 g, 1.11 mmol), prepared as described above and pentane (10 cm^3) was added. The flask was wrapped with aluminium foil and diethyl sulfide (0.110 g, 1.22 mmol, 1.1 equivalents) was added. The grey-white solid dissolved immediately. The reaction solution was placed in a freezer at −30 °C for 1 h and a needle-like crystalline product formed. Removal of the solvent by filtration gave 0.39 g (89% yield) of $[Ag(hfacac)(SEt_2)]$.

$[Ag(hfacac)L]$ (L = SMe_2, SPr^n_2 *or* SBu^n_2). These compounds were synthesised by method A except where specifically indicated.

$[Ag(hfacac)(SMe_2)]$. Colourless needles. Yield: 92.3%. M.p. 126–128 °C. IR (KBr disc): 2984w, 2932w, 2839w, 1670s, 1526s, 1315w, 1257s, 1205s, 1145s, 792m, 662m and 557m cm^{-1}. NMR (C_6D_6): ^1H, δ 6.29 (s, 1 H, CH of hfacac) and 1.23 (s, 6 H, CH_3 of SMe_2); $^{13}C-\{^1H\}$, δ 177.4 (q, *J* 32.1 Hz, C=O of hfacac), 87.2 (s, CH of hfacac) and 20.1 (s, CH_3 of SMe_2) (Found: C, 22.10; H, 1.75. Calc. for $C_7H_7AgF_6O_2$: C, 22.30; H, 1.85%).

$[Ag(hfacac)(SPr^n_2)]$. Colourless liquid. Yield: 84%. IR (KBr disc): 2970m, 2936m, 2878m, 1651s, 1522s, 1382w, 1255s, 1197s, 1143s, 1081w, 792m, 662m and 578w cm^{-1}. NMR (C_6D_6): ^1H, δ 6.26 (s, 1 H, CH of hfacac), 1.88 (t, 4 H, *J* 7.4, SCH_2 of SPr^n_2), 1.17 (m, 4 H, *J* 7.4, CH_2CH_3 of SPr^n_2) and 0.63 (t, 6 H, *J* 7.4 Hz, CH_2CH_3 of SPr^n_2); $^{13}C-\{^1H\}$, δ 177.5 (q, C=O of hfacac), 87.3 (s, CH of hfacac), 36.3 (s, SCH_2 of SPr^n_2), 23.4 (s, CH_2CH_3 of SPr^n_2) and 13.1 (s, CH_2CH_3 of SPr^n_2) (Found: C, 30.70; H, 3.65. Calc. for $C_{11}H_{15}AgF_6O_2S$: C, 30.65; H, 3.50%).

$[Ag(hfacac)(SBu^n_2)]$. Colourless liquid. Yield: 91.6%. IR (KBr disc): 2965m, 2935m, 2876m, 1655s, 1520s, 1382w, 1312w, 1254s, 1197s, 1142s, 1080m, 791m, 663m and 578m cm^{-1}. NMR: ^1H, δ 6.29 (s, 1 H, CH of hfacac), 1.94 (t, 4 H, *J* 7.3, CH_2S of SBu^n_2), 1.17 (m, 4 H, $J \approx 7$, CH_2 of SBu^n_2), 1.04 (m, 4 H, $J \approx 7$, CH_2 of SBu^n_2) and 0.73 (t, 6 H, *J* 7.1 Hz, CH_3 of SBu^n_2); $^{13}C-\{^1H\}$, δ 177.4 (q, *J* 32.1 Hz, C=O of hfacac), 87.2 (s, CH of hfacac), 34.4 (s, SCH_2 of SBu^n_2), 32.1 (s, SCH_2CH_2 of SBu^n_2), 22.0 (s, CH_2CH_3 of SBu^n_2) and 13.5 (s, CH_2CH_3 of SBu^n_2) (Found: C, 34.35; H, 4.65. Calc. for $C_{13}H_{19}AgF_6O_2$: C, 33.85; H, 4.15%).

$[Ag(hfacac)(C_4H_8OS)]$. The synthetic method was similar to method A, the only difference being the ratio of reactants. Silver(I) oxide (0.70 g 3.02 mmol) was treated with Hhfacac (1.39 g, 6.63 mmol, 1.10 equivalents) then 1,4-oxathiane (C_4H_8OS) (0.65 g, 6.24 mmol, 1.03 equivalents) was added. The reaction solution was filtered after 3 h. Removal of the volatile components *in vacuo* gave 2.23 g (88% yield) of a white solid. A portion of the crude product (350 mg) was recrystallized from diethyl ether–pentane (2 cm^3 : 10 cm^3) solution at −30 °C and 285 mg of colourless product obtained (yield 81.4%). M.p. 85–87 °C. IR (KBr disc): 2933w, 2856w, 1661s, 1522s, 1506s, 1255s, 1200s, 1139s, 1102w, 794m, 661m and 579m cm^{-1}. NMR (C_6D_6): ^1H, δ 6.32 (s, 1 H, CH of hfacac), 3.28 (t, 4 H, *J* 4.8, CH_2O of C_4H_8OS) and 1.59 (t, 4 H, *J* 4.8, CH_2S of C_4H_8OS); $^{13}C-\{^1H\}$, δ 177.6 (q, *J* 32.1, C=O of hfacac), 118.6 (q, *J* 289.3 Hz, CF_3 of hfacac), 87.4 (s, CH of hfacac), 68.5 (s, CH_2O of C_4H_8OS) and 28.5 (s, CH_2S of C_4H_8OS) (Found: C, 25.65; H, 2.25. Calc. for $C_9H_9AgF_6O_3$: C, 25.80; H, 2.15%).

$[Ag(hfacac)(C_4H_8OS)_2]$. The following reagents were mixed in a Schlenk flask: Ag_2O (0.70 g, 3.02 mmol), Hhfacac (1.39 g, 6.64 mmol, 1.1 equivalents) and 1,4-oxathiane (1.55 g, 14.19 mmol, 2.40 equivalents). Other conditions were as those for $[Ag(hfacac)(C_4H_8OS)]$. A white solid product was obtained (2.23 g, 88% yield), which was dissolved in diethyl ether (*ca.* 5 cm^3) and cooled at −30 °C to give 1.56 g (≈61% yield) of a colourless crystalline product. M.p. 61–62 °C. IR (KBr disc): 2954w, 2923w, 1669s, 1522s, 1314w, 1257s, 1201s, 1140s, 791s, 654m and 571m cm^{-1}. NMR (C_6D_6): ^1H, δ 6.31 (s, 1 H, CH of hfacac), 3.47 (t, 8 H, *J* 4.8, CH_2O of C_4H_8OS) and 1.94 (t, 8 H, *J* 4.8, CH_2S of C_4H_8OS); $^{13}C-\{^1H\}$ δ 177.5 (q, *J* 31.5, C=O of hfacac), 121.3 (q, *J* 298.0 Hz, CF_3 of hfacac), 87.1 (s, CH of hfacac), 68.5 (s, CH_2O of C_4H_8OS) and 28.3 (s, CH_2S of C_4H_8OS) (Found: C, 29.80; H, 3.60. Calc. for $C_{13}H_{17}AgF_6O_4S_2$: C, 29.85; H, 3.25%).

$[\{Ag(hfacac)\}_2(nbd)]$. The synthetic method used was similar to method A. Silver(I) oxide (1.40 g, 6.04 mmol) was treated with Hhfacac (2.57 g, 12.35 mmol, 1.02 equivalents) then nbd (0.65 g, 7.05 mmol, 0.58 equivalent) was added. After 5 h the reaction mixture was filtered. Removal of volatile components gave 3.96 g (90% crude yield) of white solid product which was recrystallized from diethyl ether (*ca.* 10 cm^3) at −30 °C to give a colourless crystalline product, 2.56 g (58% yield). M.p. ≈130 °C (decomp.). IR (KBr disc): 3857m, 3738w, 2931w, 2350w, 1659s, 1524s, 1486s, 1314w, 1255s, 1201s, 1142s, 873s, 792s, 657s and 571s cm^{-1}. NMR (C_6D_6): ^1H, δ 6.31 (t, 4 H, *J* 1.8, CH=CH of nbd), 6.18 (s, 2 H, CH of hfacac), 3.08 (m, 2 H, *J* ≈1.6, CH of nbd) and 1.59 (t, 2 H, *J* 1.6, CH_2 of nbd); $^{13}C-\{^1H\}$, δ 177.4 (q, *J* 31.5 Hz, C=O of hfacac), 141.1 (s, CH=CH of nbd), 87.1 (s, CH of hfacac), 75.1 (s, CH of nbd) and 50.8 (s, CH_2 of nbd) (Found: C, 28.25; H, 1.40. Calc. for $C_{17}H_{10}Ag_2F_{12}O_4$: C, 28.30; H, 1.50%).

Alternatively, the reactants were added in the following way: silver(I) oxide (1.40 g, 6.04 mmol) was treated with nbd (0.65 g, 7.05 mmol) first. Then Hhfacac (2.60 g, 1.24 mmol) was added. Other conditions were as before. After removal of the volatile components, 4.07 g of a white solid product was obtained, which exhibited a ^{1}H NMR spectrum analogous to that described above. Crystals grown from a diethyl ether solution at −30 °C were shown to have the same unit-cell parameters as those of the product prepared as before, as determined by single-crystal and powder X-ray diffraction.

X-Ray Crystallographic Studies.—Single-crystal X-ray diffraction studies of $[\text{Ag(hfacac)}(\text{C}_4\text{H}_8\text{OS})_2]$, $[\{\text{Ag(hfacac)}\}_2(\text{nbd})]$ and $[\{\text{Ag(hfacac)}\}_2(\text{H}_2\text{O})]$ were carried out using a Nicolet R3 m/v diffractometer. A summary of the crystal data and experimental details is presented in Table 1. A general description of the experimental procedure is presented here, with more details available as supplementary material. The crystallographic data were obtained at 293 K with a range 2θ 3.0–55.0° with ω scans. In general, the structures were solved by direct methods using SHELXTL PLUS[43] and refined by full-matrix least squares. The non-hydrogen atoms were located through this and Fourier-difference calculations. Details of the refinement are given below for each individual structure.

Crystals of $[\text{Ag(hfacac)}(\text{C}_4\text{H}_8\text{OS})_2]$ and $[\{\text{Ag(hfacac)}\}_2(\text{nbd})]$ were grown from diethyl ether solution at −30 °C, those of $[\{\text{Ag(hfacac)}\}_2(\text{H}_2\text{O})]$ from methylene chloride at 0 °C. Suitable crystals were selected and sealed in a glass capillary tube for $[\{\text{Ag(hfacac)}\}_2(\text{nbd})]$ or attached to the tip of a glass fibre with grease for the other compounds.

$[\text{Ag(hfacac)}(\text{C}_4\text{H}_8\text{OS})_2]$. Refinement of all non-hydrogen atoms showed that the fluorines had some positional disorder and a two-fold disorder model was used for fluorine sites on CF_3 groups C(4) and C(5). The two sets of F atoms were allowed to vary in position with their occupation factors fixed to x (primary position) or $1 - x$ (secondary position). Primary and secondary F atoms had the same isotropic U rates which were allowed to vary. The final model comprised anisotropic refinement of all non-hydrogen atoms except the F atoms and all hydrogen atoms were included in idealized positions (riding model) with isotropic U set to 1.25 $U_{\text{equiv.}}$ of the parent atom.

$[\{\text{Ag(hfacac)}\}_2(\text{nbd})]$. Refinement of all non-hydrogen atoms showed that one CF_3 group C(4) exhibited some disorder. This was represented by two sites where the disordered atoms shared common isotropic U and the occupancy of x for one set was varied while the occupancy of other was fixed at $1 - x$. In the final model all non-hydrogen atoms were treated anisotropically. Hydrogen atoms were included in idealized positions (riding model) with isotropic U set to 1.25 $U_{\text{equiv.}}$ of the parent atom.

$[\{\text{Ag(hfacac)}\}_2(\text{H}_2\text{O})]$. Refinement with all non-hydrogen atoms anisotropic gave a difference map consistent with disorder about the CF_3 groups on C(5) and C(10) for which no simple model could be discerned. The map also revealed electron density at the position expected for one hydrogen atom bonded to O(5) in the co-ordinated water molecule and for the hydrogen atoms of C(2) and C(7). The final refinement cycle included all non-hydrogen atoms anisotropic, H(2), H(7) and H(5a) isotropic and H(5b) fixed. It is noteworthy that the crystal used changed from a colourless prism to a dark colour with concomitant reduction in intensity of 7% in the standard reflection used to monitor the crystal integrity during the data collection.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Results and Discussion

Syntheses and Characterization.—The air- and moisture-stable compounds $[\{\text{Ag(hfacac)}\}_m\text{L}_n]$ (L = nbd, $m = 2, n = 1$; L = SMe_2, SEt_2, $\text{SPr}^n{}_2$ or $\text{SBu}^n{}_2$, $m = 1, n = 1$; L = $\text{C}_4\text{H}_8\text{OS}$, $m = 1$, $n = 1$ or 2) were prepared by reaction of the appropriate Lewis bases with $[\{\text{Ag(hfacac)}\}_2(\text{H}_2\text{O})]$ (generated by addition of 2 equivalents Hhfacac to Ag_2O) as shown in equations (1) and (2). This method resulted in high yields of

$$2\text{Hhfacac} + \text{Ag}_2\text{O} \xrightarrow[-20\,°\text{C}]{\text{ether}} [\{\text{Ag(hfacac)}\}_2(\text{H}_2\text{O})] \quad (1)$$

$$\frac{m}{2}[\{\text{Ag(hfacac)}\}_2(\text{H}_2\text{O})] + n\text{L} \xrightarrow[-20\,°\text{C}]{\text{ether}} [\{\text{Ag(hfacac)}\}_m\text{L}_n] + \frac{m}{2}\text{H}_2\text{O} \quad (2)$$

the corresponding silver(I) complexes. After the reactions were complete the mixtures were filtered to remove any insoluble material. Removal of the volatile components generally resulted in isolation of products which gave satisfactory elemental analyses. All compounds were characterized by solution NMR and solid-state and liquid-phase FTIR spectroscopies. The compounds $[\{\text{Ag(hfacac)}\}_2(\text{nbd})]$, $[\text{Ag(hfacac)}(\text{C}_4\text{H}_8\text{OS})]$, $[\text{Ag(hfacac)}(\text{C}_4\text{H}_8\text{OS})_2]$, $[\text{Ag(hfacac)}(\text{SEt}_2)]$ and $[\text{Ag(hfacac)}(\text{SMe}_2)]$ are white solids at room temperature. The other two compounds $[\text{Ag(hfacac)}(\text{SR}_2)]$ (R = Pr^n or Bu^n) are liquids at room temperature. Attempts to synthesise [Ag(hfacac)(nbd)] in this way by changing the ratio of reactants failed. This is consistent with the observations of Doyle *et al.*[42] who reported the synthesis of the copper(I) analogue, $[\{\text{Cu(hfacac)}\}_2(\text{nbd})]$, but were unable to prepare the complex [Cu(hfacac)(nbd)], even when an excess of the diene was used.

We also examined the effect of a different order of addition of the reactants in the synthesis of $[\{\text{Ag(hfacac)}\}_2(\text{nbd})]$ on the nature of the final product. This species was chosen because it was expected that a different order of addition might affect the extent of oligomerization of the products. In the case of the analogous copper(I) reactions the order of reagent addition is extremely important because addition of Hhfacac before the Lewis base results in rapid disproportionation of the '(hfacac)Cu' intermediate. In the case of silver(I) the product $[\{\text{Ag(hfacac)}\}_2(\text{nbd})]$ obtained by reverse addition of the Hhfacac and L reagents was identical to that obtained by reactions (1) and (2) as determined by comparison of ^{1}H NMR spectra, single-crystal and powder X-ray diffraction data.

The integrated intensities of the ^{1}H NMR spectra were consistent with the empirical formulae only when the relaxation delay was longer than 15 s. The ^{13}C-{^{1}H} NMR spectra are also consistent, however the peak of the ^{13}C resonance of the CF_3 groups was difficult to observe even when concentrated solutions, long relaxation delays and a large number of acquisitions were used. The compound $[\{\text{Ag(hfacac)}\}_2(\text{nbd})]$ exhibits ^{1}H and ^{13}C-{^{1}H} NMR spectra with a single type of olefinic and aliphatic nbd resonance. This observation is inconsistent with the solid state-single crystal X-ray diffraction data (see later), where only one carbon–carbon double bond of nbd co-ordinates to silver(I). No decoalescence of these peaks in the solution ^{1}H NMR spectra was observed even on cooling to 180 K which indicates the presence of a fast exchange process or a different solution structure. The ^{1}H NMR spectrum of $[\text{Ag(hfacac)}(\text{C}_4\text{H}_8\text{OS})_2]$ exhibits two triplets for two types of methylene groups in the 1,4-oxathiane ligand. However, the methylene protons in equatorial and axial position are expected to be chemically inequivalent in the absence of exchange processes, based on the monomeric structure determined by single-crystal X-ray diffraction in the solid state. Variable-temperature ^{1}H NMR spectroscopy showed the methylene protons next to the S atom decoalesced into two peaks. The coalescence temperature was about 210 K, with Δν = 196 Hz in the absence of exchange giving an approximate activation barrier for inversion of $\Delta G^\ddagger \approx 10$ kcal mol^{-1} (*ca.* 41.84 kJ mol).[44] However the two protons on the methylene nearest to the O atom could not be distinguished even on cooling to 194 K, although some broadening was observed. These observations are consistent with the solid-state structural data which show that the 1,4-oxathiane ligand is co-ordinated to the silver(I) centre *via* the S atom which may be responsible for the greater chemical shift difference between the axial and equatorial protons adjacent to S compared to the methylene protons adjacent to O.

In order better to understand the nature of the reactions (1) and (2), we isolated and characterized the species previously described as '(hfacac)Ag'.[29,42] The structural investigation of this species is also interesting because the corresponding copper(I) complex is unstable with respect to disproportionation. However, the compound isolated was analysed not as '(hfacac)Ag', but as [{Ag(hfacac)}$_2$(H$_2$O)], a white powder, stable to air, which can be crystallized from methylene chloride at 0 °C.

For all the compounds described above the solution-phase ^{1}H and ^{13}C NMR and the solid-state IR spectral data[45] were consistent with chelation through both oxygen atoms in these phases based on the chemical shift of the hfacac methine proton and carbon.[36,45]

To determine whether these [{Ag(hfacac)}$_m$L$_n$] species are suitable as precursors for the CVD of silver films, sublimation experiments were carried out at 50 mTorr (*ca.* 6.65 Pa) and 80–90 °C. Where L = SMe$_2$ or SEt$_2$, $m = 1$, $n = 1$ and L = C$_4$H$_8$OS, $m = 1$, $n = 1$ or 2, attempted sublimation was associated with thermal decomposition. Powder X-ray diffraction analysis of the dark, unsublimed residues showed that crystalline silver was formed. Furthermore, the material collected on the cold-finger did not correspond to the starting materials. As a result it is unlikely that these species will be suitable as precursors for the CVD of Ag using conventional precursor-delivery methods which require heating of the precursor for extended periods to generate suitable precursor partial pressures. However, these species are suitable for aerosol-assisted CVD (AACVD) of silver films where the aerosol-delivery method enables a high precursor transport rate to the substrate but does not require high precursor vapour pressure and can accommodate precursors of low thermal stability.[39]

Solid-state Single-crystal Structures.—The solid-state structures of [Ag(hfacac)(C$_4$H$_8$OS)$_2$], [{Ag(hfacac)}$_2$(nbd)] and [{Ag(hfacac)}$_2$(H$_2$O)] were determined by single-crystal X-ray diffraction, Figs. 1–3, respectively. Selected bond lengths and angles are listed in Tables 2–4, atomic coordinates in Table 5.

The species [Ag(hfacac)(C$_4$H$_8$OS)$_2$] is monomeric in the solid state with a distorted-tetrahedral silver(I) geometry, see Fig. 1. The structural features are similar to those reported recently for [Ag(hfacac)(PMe$_3$)$_2$].[29,30] The S–Ag–S angle of 149.6(1)° is significantly larger than the tetrahedral angle, but smaller than P–Ag–P [159.4(2)°] of [Ag(hfacac)(PMe$_3$)$_2$]. The O–Ag–O bite angle of the hfacac ligands is larger [74.4(2)°] than for [Ag(hfacac)(PMe$_3$)$_2$] [70.3(7)°], but smaller than those of other (β-diketonato)bis(ligand)copper compounds.[30,36] This observation is consistent with the tendency of silver(I) to form linear AgL$_2$ units with neutral ligands. The O–Ag bond lengths are slightly asymmetric, both shorter than those observed for [Ag(hfacac)(PMe$_3$)$_2$] [2.45(2)–2.64(2) Å], but similar to those observed for [{Ag(hfacac)(cod)}$_2$].[30,38] It is interesting that the two sulfur atoms are co-ordinated to the silver centre *via* their axial rather than equatorial lone pairs.

The structure of [{Ag(hfacac)}$_2$(nbd)] is dimeric with four silver atoms per formula unit, see Fig. 2(*a*). There are two kinds of silver(I) atoms in each molecule; one co-ordinates to the C=C bond of nbd and three O atoms of hfacac and the other only to the O atoms of hfacac ligands. Each is four-co-ordinate. The Ag–O distances are similar to those found in other [M(hfacac)L$_n$] compounds. There exist two types of hfacac co-ordination mode, namely tridentate μ bridging and tetradentate μ$_3$ bridging which are similar to those observed in [{Ag(hfacac)(cod)}$_2$]. The molecular structure shows that only one carbon–carbon double bond of the nbd ligand interacts strongly with silver(I). The bond lengths C(11)–C(12) 1.339(11), Ag(2)–C(11) 2.356(9) and Ag(2)–C(12) 2.373(8) Å show this

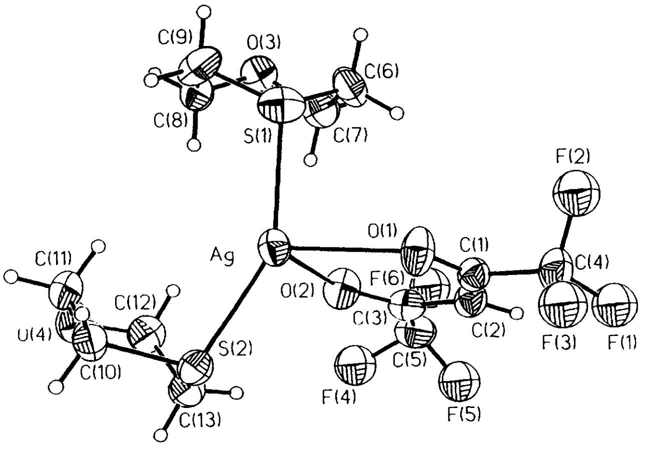

Fig. 1 An ORTEP[46] plot for [Ag(hfacac)(C$_4$H$_8$OS)$_2$] showing the molecular structure with the atom-numbering scheme

Table 1 Summary of crystal data and experimental details*

	[Ag(hfacac)(C$_4$H$_8$OS)$_2$]	[{Ag(hfacac)}$_2$(nbd)]	[{Ag(hfacac)}$_2$(H$_2$O)]
Empirical formula	C$_{13}$H$_{17}$AgF$_6$O$_4$S$_2$	C$_{17}$H$_{10}$Ag$_2$F$_{12}$O$_4$	C$_{10}$H$_4$Ag$_2$F$_{12}$O$_5$
M	523.26	721.98	647.9
Colour, habit	Colourless, transparent prism	Colourless, transparent block	Colourless, transparent block
a/Å	9.4675(9)	9.071(2)	9.338(1)
b/Å	11.3448(9)	11.542(1)	10.018(1)
c/Å	11.3993(9)	11.542(1)	10.343(1)
α/°	108.708(6)	105.88(1)	98.12(1)
β/°	101.754(7)	97.14(1)	103.90(1)
γ/°	113.559(7)	108.45(1)	113.36(1)
U/Å^3	981.01(14)	1072.7(4)	831.35(11)
Crystal size/mm	0.253 × 0.322 × 0.506	0.185 × 0.345 × 0.690	0.184 × 0.230 × 0.460
D_c/g cm^{-3}	1.771	2.235	2.588
Reflections collected	8542	7434	5742
Reflections used	3181	2775	2553
μ/mm^{-1}	1.309	1.952	2.506
R	0.0565	0.0471	0.0395
R'	0.0656	0.0508	0.0433

* Details in common: triclinic, space group $P\bar{1}$; 293 K; λ = 0.710 73 Å; $Z = 2$; $R = \Sigma\Delta F/\Sigma F_o$; $R' = \Sigma w^{\frac{1}{2}}\Delta F/\Sigma w^{\frac{1}{2}}F_o$ where $\Delta F = |F_o - F_c|$.

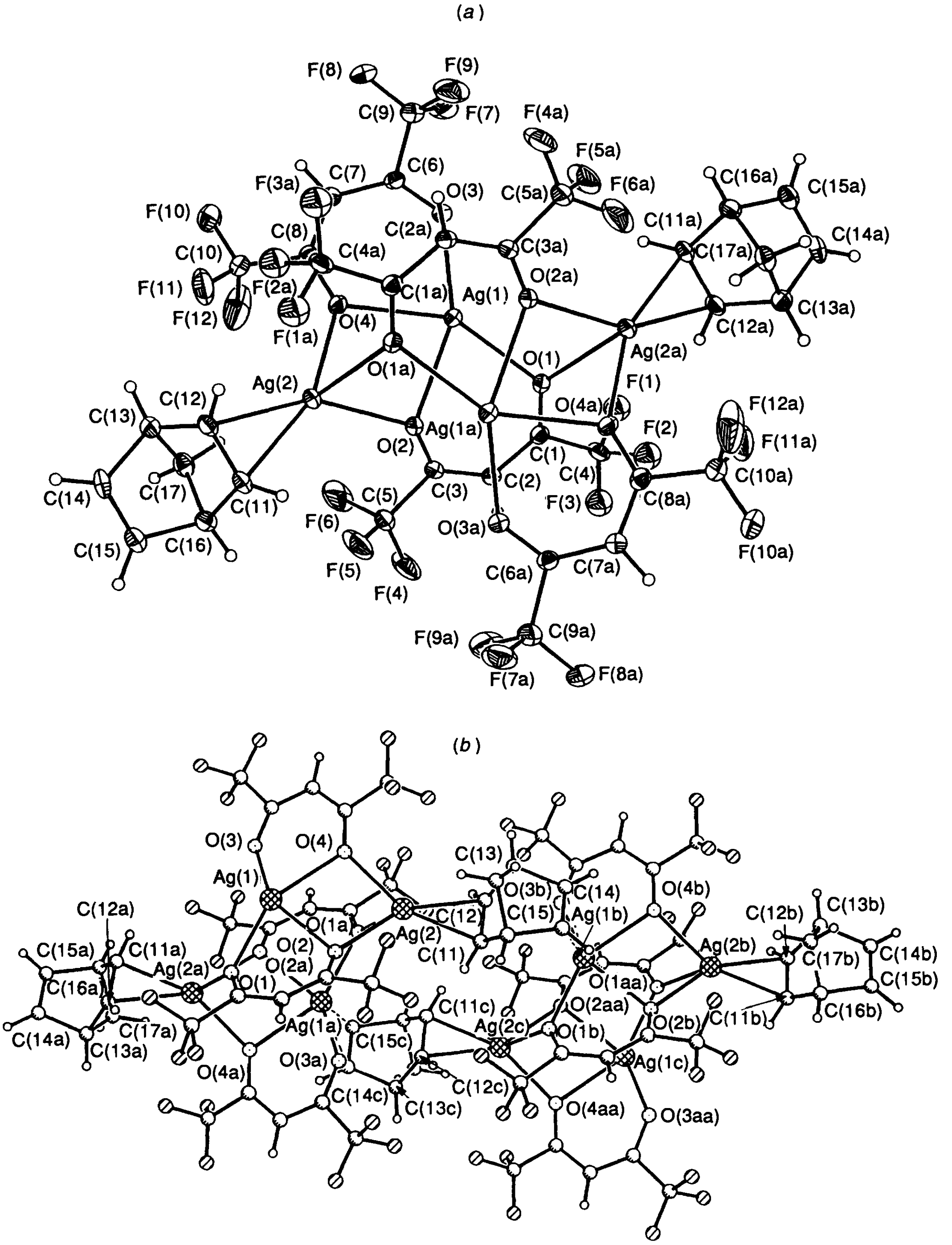

Fig. 2 (*a*) An ORTEP[46] plot for [{Ag(hfacac)}$_2$(nbd)] showing the molecular structure with the atom-numbering scheme. (*b*) Ball-and-stick drawing of the crystal structure emphasizing the interaction of the 'unco-ordinated' carbon–carbon double bond with a silver(I) in an adjacent asymmetric unit

double bond is strongly co-ordinated to Ag, while C(14)–C(15) 1.322(13), C(14)–Ag(1a) 2.856 and C(15)–Ag(1a) 2.821 Å show that the other is more weakly co-ordinated to an Ag atom in an adjacent molecule, see Fig. 2(*b*). The double-bond lengths are similar to those in [{CuCl(nbd)}$_4$] [1.345(11)–1.317(11) Å] where also only one double bond of a nbd ligand co-ordinated to the copper(I) centre.[47] The C=C bond length in free nbd is 1.343 Å as determined by gas-phase electron diffraction[48] and indicates that the silver(I) centre acts only as a π-electron acceptor and not an electron donor towards Ag^I as has been observed previously in the case of similar copper complexes.[34] The sum of the covalent radii for Ag^I and sp^2-hybridized carbon is 2.19 Å, while the sum of the van der Waals radii for this pair is 3.29 Å.[49] Therefore, it is likely that there is a weak intermolecular interaction between C(14)=C(15) and Ag(1a) which results in the formation of a three-dimensional network in the solid state.

For [{Ag(hfacac)}$_2$(H$_2$O)] there are two silver atoms and two hfacac ligands in one asymmetric unit, see Fig. 3(*a*). Each hfacac ligand is co-ordinated to silver(I) in a tridentate μ bridging fashion by O atoms. The water molecule is bonded to Ag(2). The Ag–O bond lengths to the hfacac ligands are similar to those observed in other [Ag^I(hfacac)L] complexes[29,38] but longer than the normal covalent Ag^I–O bond length of *ca.* 2.2 Å. However, Ag(2)–O(5), (H$_2$O) 2.263(6) Å is shorter than the Ag–O bond distance to the hfacac ligands. There are two

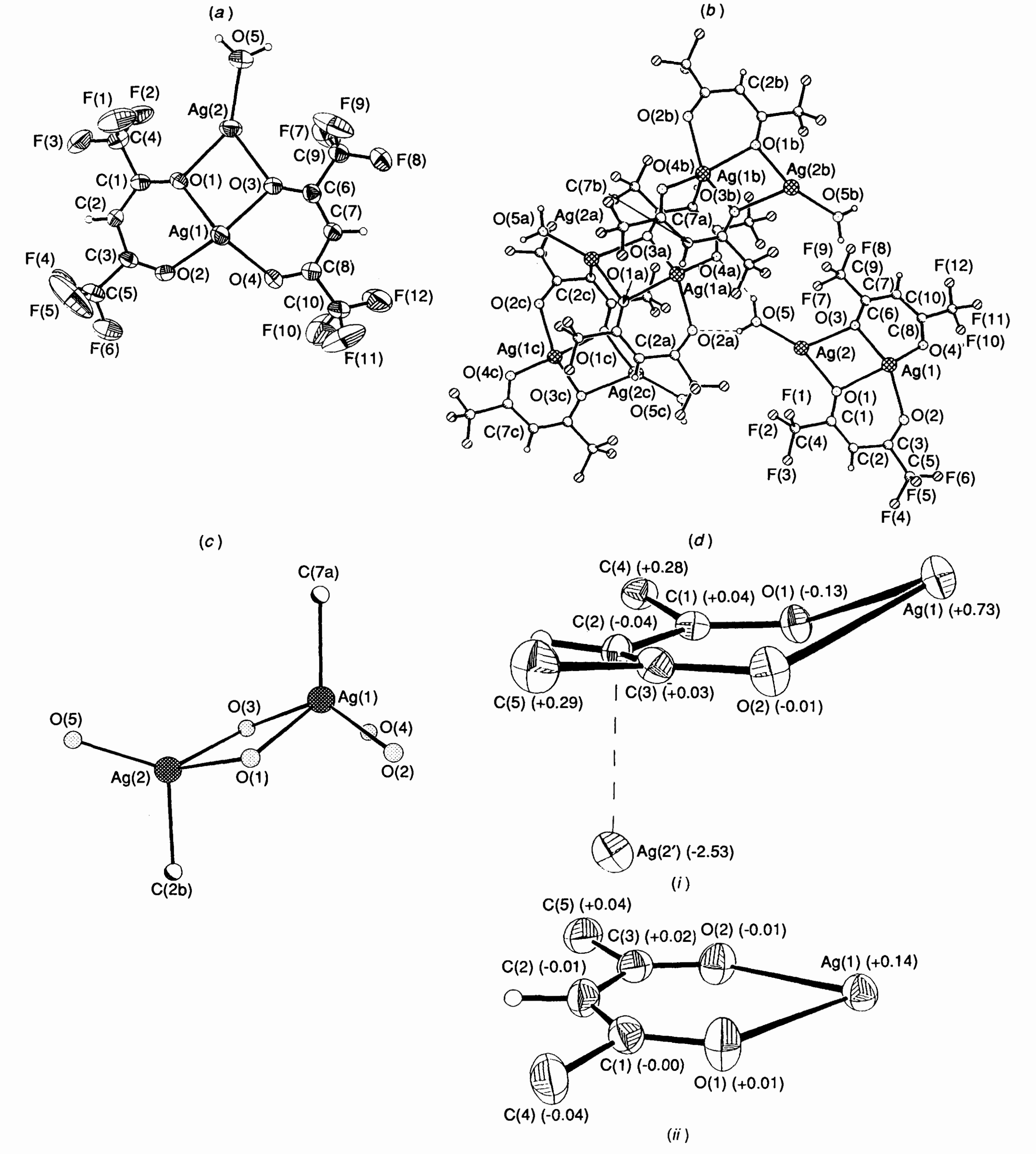

Fig. 3 (*a*) An ORTEP[46] plot for [$\{Ag(hfacac)\}_2(H_2O)$] showing the molecular structure with the atom-numbering scheme. (*b*) Ball-and-stick drawing of the crystal structure emphasizing the three-dimensional network structure with C–Ag bonds and hydrogen bonding between the asymmetric units. Symmetry relationships: a $x - 1, y, z$; b $-1 - x, -y, -z$; c $-1 - x, -y, 1 - z$. (*c*) Ball-and-stick drawing emphasizing the co-ordination environment of silver atom C(2a) at $-x, -y, -z$ and C(2b) at $-x, -y, 1 - z$. (*d*) The ORTEP[46] plots of (hfacac)Ag ring (*i*) in [$\{Ag(hfacac)\}_2(H_2O)$] and (*ii*) in [$Ag(hfacac)(C_4H_8OS)_2$] for comparison of the degree of distortion

noteworthy intermolecular Ag–C interactions, C(7)–Ag(1a) 2.391(6) and C(2)–Ag(2a) 2.492(6) Å, see Fig. 3(*b*). These distances are similar to those found between the olefin carbon and silver atoms in [$\{Ag(hfacac)\}_2(nbd)$] [Fig. (2(*b*)]. An analogous interaction between co-ordinated β-diketonate methine carbons and another metal centre also was found in some [$Pt^{IV}R_2(acac)_2$] complexes (acac = acetylacetonate).[50–53] The present intermolecular distances are slightly longer than those observed in [NBu_4][$Pd_2Ag(C_6F_5)(acac)_2$][54] [2.237(7) Å] but similar to those for [$AgNi(acac)_3$]·$2AgNO_3$·H_2O (2.34 ± 0.09 Å).[55] In [$\{Ag(hfacac)\}_2(H_2O)$] these C–Ag bonds form along the *c* axis of the crystal and make the compounds

Table 2 Selected bond lengths (Å) and angles (°) for [Ag(hfacac)(C_4H_8OS)$_2$]

Ag–S(1)	2.468(2)	Ag–S(2)	2.473(2)
Ag–O(1)	2.477(7)	Ag–O(2)	2.400(7)
S(1)–C(6)	1.821(9)	S(1)–C(9)	1.771(10)
S(2)–C(10)	1.828(10)	S(2)–C(13)	1.829(10)
O(1)–C(1)	1.250(10)	O(2)–C(3)	1.238(11)
C(1)–C(2)	1.383(11)	C(1)–C(4)	1.504(14)
C(3)–C(2)	1.392(13)	C(3)–C(5)	1.517(14)
O(3)–C(7)	1.420(11)	O(3)–C(8)	1.411(11)
O(4)–C(11)	1.406(12)	O(4)–C(12)	1.387(13)
C(6)–C(7)	1.462(14)	C(8)–C(9)	1.499(14)
C(10)–C(11)	1.457(9)	C(12)–C(13)	1.462(10)

S(1)–Ag–S(2)	149.6(1)	S(1)–Ag–O(1)	88.3(2)
S(2)–Ag–O(1)	117.8(1)	S(1)–Ag–O(2)	109.5(1)
S(2)–Ag–O(2)	93.4(2)	O(1)–Ag–O(2)	74.4(2)
Ag–S(1)–C(6)	104.1(3)	Ag–S(1)–C(9)	111.9(4)
C(6)–S(1)–C(9)	97.6(4)	Ag–S(2)–C(10)	106.8(3)
Ag–S(2)–C(13)	104.3(3)	C(10)–S(2)–C(13)	97.6(5)
Ag–O(1)–C(1)	129.9(6)	Ag–O(2)–C(3)	132.4(6)
O(1)–C(1)–C(2)	129.1(8)	O(1)–C(1)–C(4)	112.8(7)
C(2)–C(1)–C(4)	118.1(7)	O(2)–C(3)–C(5)	113.0(9)
C(1)–C(2)–C(3)	124.6(8)	S(1)–C(6)–C(7)	112.0(7)
O(2)–C(3)–C(2)	129.2(8)	S(2)–C(13)–C(12)	111.0(7)
S(1)–C(9)–C(8)	112.2(7)	S(2)–C(10)–C(11)	111.3(6)
C(2)–C(3)–C(5)	117.8(8)		

Table 3 Selected bond lengths (Å) and angles (°) for [{Ag(hfacac)}$_2$(nbd)]

Ag(1)–O(1)	2.371(4)	Ag(1)–O(2)	2.495(6)
Ag(1)–O(3)	2.300(6)	Ag(1)–O(4)	2.454(4)
O(1)–C(1)	1.257(10)	O(1)–Ag(2a)	2.575(6)
C(1)–C(2)	1.382(11)	C(1)–C(4)	1.525(10)
C(3)–C(2)	1.366(10)	C(3)–C(5)	1.534(13)
O(2)–C(3)	1.267(10)	O(3)–C(6)	1.244(8)
C(6)–C(7)	1.400(10)	C(6)–C(9)	1.540(13)
C(8)–C(7)	1.377(12)	C(8)–O(4)	1.253(9)
C(8)–C(10)	1.521(10)	O(4)–Ag(2)	2.310(6)
Ag(2)–C(11)	2.356(9)	Ag(2)–C(12)	2.373(8)
Ag(2)–O(1a)	2.575(6)	Ag(2)–O(2)	2.377(5)
C(11)–C(12)	1.339(11)	C(14)–C(15)	1.322(13)

O(1)–Ag(1)–O(2)	73.5(2)	O(1)–Ag(1)–O(3)	132.7(2)
O(2)–Ag(1)–O(3)	145.9(2)	O(1)–Ag(1)–O(4)	149.3(2)
O(2)–Ag(1)–O(4)	75.8(2)	O(3)–Ag(1)–O(4)	76.1(2)
Ag(1)–O(1)–C(1)	124.6(4)	Ag(1)–O(1)–Ag(2a)	102.0(2)
C(1)–O(1)–Ag(2a)	132.3(4)	O(1)–C(1)–C(2)	128.0(7)
O(1)–C(1)–C(4)	114.8(7)	C(2)–C(1)–C(4)	117.3(7)
C(1)–C(2)–C(3)	125.2(8)	O(2)–C(3)–C(2)	128.4(8)
C(2)–C(3)–C(5)	117.5(7)	O(2)–C(3)–C(5)	114.1(6)
Ag(1)–O(2)–C(3)	120.1(5)	Ag(1)–O(2)–Ag(2)	97.2(2)
C(3)–O(2)–Ag(2)	135.8(5)	Ag(1)–O(3)–C(6)	129.0(5)
O(3)–C(6)–C(7)	129.3(8)	O(3)–C(6)–C(9)	113.1(7)
C(7)–C(6)–C(9)	117.6(6)	C(6)–C(7)–C(8)	124.4(6)
C(7)–C(8)–O(4)	128.2(6)	C(7)–C(8)–C(10)	117.2(6)
O(4)–C(8)–C(10)	114.6(7)	Ag(1)–O(4)–C(8)	124.3(5)
Ag(1)–O(4)–Ag(2)	100.1(2)	C(8)–O(4)–Ag(2)	134.8(5)
O(2)–Ag(2)–O(4)	80.9(2)	O(2)–Ag(2)–C(11)	119.4(2)
O(4)–Ag(2)–C(11)	157.6(2)	O(2)–Ag(2)–C(12)	152.3(2)
O(4)–Ag(2)–C(12)	126.3(2)	C(11)–Ag(2)–C(12)	32.9(3)
O(2)–Ag(2)–O(1a)	78.8(2)	O(4)–Ag(2)–O(1a)	76.6(2)
C(11)–Ag(2)–O(1a)	114.6(3)	C(12)–Ag(2)–O(1a)	109.8(3)
Ag(2)–C(11)–C(12)	74.2(5)	Ag(2)–C(12)–C(11)	72.9(5)
Ag(2)–C(12)–C(13)	115.3(7)	Ag(2)–C(11)–C(16)	114.9(6)

Table 4 Selected bond lengths (Å) and angles (°) for [{Ag(hfacac)}$_2$(H_2O)]

Ag(1)–O(1)	2.400(4)	Ag(1)–O(2)	2.346(4)
Ag(1)–O(3)	2.414(3)	Ag(1)–O(4)	2.419(5)
Ag(1)–C(7a)	2.391(6)	Ag(2)–O(1)	2.441(3)
Ag(2)–O(3)	2.415(4)	Ag(2)–O(5)	2.263(6)
Ag(2)–C(2a)	2.492(6)	O(1)–C(1)	1.244(5)
O(2)–C(3)	1.237(6)	O(3)–C(6)	1.249(6)
O(4)–C(8)	1.228(5)	C(1)–C(2)	1.405(7)
C(1)–C(4)	1.541(10)	C(3)–C(2)	1.412(9)
C(2)–Ag(2a)	2.492(6)	C(3)–C(5)	1.533(7)
C(6)–C(7)	1.394(9)	C(6)–C(9)	1.535(7)
C(8)–C(7)	1.427(8)	C(7)–Ag(1a)	2.391(6)
C(8)–C(10)	1.538(11)		

O(1)–Ag(1)–O(2)	76.8(1)	O(1)–Ag(1)–O(3)	76.9(1)
O(2)–Ag(1)–O(3)	134.6(1)	O(1)–Ag(1)–O(4)	127.3(1)
O(2)–Ag(1)–O(4)	92.5(1)	O(3)–Ag(1)–O(4)	75.4(1)
O(1)–Ag(1)–C(7a)	122.0(2)	O(2)–Ag(1)–C(7a)	120.8(1)
O(3)–Ag(1)–C(7a)	104.4(1)	O(4)–Ag(1)–C(7a)	107.8(2)
O(1)–Ag(2)–O(3)	76.1(1)	O(1)–Ag(2)–O(5)	133.3(2)
O(3)–Ag(2)–O(5)	124.0(2)	O(1)–Ag(2)–C(2a)	104.1(2)
O(3)–Ag(2)–C(2a)	103.8(2)	O(5)–Ag(2)–C(2a)	109.4(2)
Ag(1)–O(4)–Ag(2)	102.7(1)	Ag(1)–O(1)–C(1)	124.6(3)
Ag(2)–O(1)–C(1)	132.7(4)	Ag(1)–O(2)–C(3)	125.9(4)
Ag(1)–O(1)–C(1)	124.6(4)	Ag(1)–O(1)–Ag(2a)	102.0(2)
Ag(1)–O(3)–Ag(2)	103.0(1)	Ag(1)–O(3)–C(6)	124.9(4)
Ag(2)–O(3)–C(6)	132.0(3)	Ag(1)–O(4)–C(8)	125.4(4)
O(1)–C(1)–C(2)	128.4(6)	O(1)–C(1)–C(4)	114.7(5)
C(1)–C(2)–C(3)	123.7(4)	C(2)–C(1)–C(4)	116.9(4)
C(1)–C(2)–Ag(2a)	94.6(4)	C(3)–C(2)–Ag(2a)	96.1(4)
O(2)–C(3)–C(2)	128.0(4)	C(6)–C(7)–Ag(1a)	93.5(4)
O(2)–C(3)–C(5)	116.0(5)	C(2)–C(3)–C(5)	115.1(5)
O(3)–C(6)–C(7)	129.0(5)	O(3)–C(6)–C(9)	113.2(5)
C(7)–C(6)–C(9)	117.8(4)	C(6)–C(7)–C(8)	123.6(4)
C(8)–C(7)–Ag(1a)	99.0(4)	O(4)–C(8)–C(7)	128.8(6)
O(4)–C(8)–C(10)	114.6(5)	C(7)–C(8)–C(10)	116.6(4)

oligomeric in the solid state. The water molecule is also hydrogen bonded to the hfacac oxygens of an adjacent molecule along the *a* axis of the crystal [see Fig. 3(*b*)]. Therefore one silver atom has approximately tetrahedral geometry and the other distorted square-pyramidal geometry, as shown in Fig. 3(*c*). Owing to the interaction of the silver atoms with C(2) and C(7), the sp^2 hybridization of the methine carbons in hfacac ligand should be distorted towards sp^3 hybridization. As a result, the (hfacac)Ag ring deviates from planarity and a comparison of this distorted conformation with the planar conformation found in [Ag(hfacac)(C_4H_8OS)$_2$] is presented in Fig. 3(*d*).

Conclusion

The reaction of Ag_2O with Hhfacac results in the formation of [{Ag(hfacac)}$_2$(H_2O)]. This was treated with other Lewis-base donors to displace the water molecule and form [{Ag(hfacac)}$_m$L$_n$] (L = nbd, $m = 2$, $n = 1$; L = SMe_2, SEt_2, $SPr^n{}_2$ or $SBu^n{}_2$, $m = 1, n = 1$; L = 1,4-oxathiane, $m = 1, n =$ 1 or 2). The solid-state structures of three of these molecules were determined by single-crystal X-ray diffraction. The complex [Ag(hfacac)(C_4H_8OS)$_2$] is monomeric in the solid state with a distorted-tetrahedral silver(I) geometry. The species [{Ag(hfacac)}$_2$(nbd)] is dimeric with four silver atoms in the formula unit. Each molecule is weakly intermolecularly co-ordinated through Ag···C=C interactions. The structure of [{Ag(hfacac)}$_2$(H_2O)] shows that it consists of non-planar hfacac rings which are intermolecularly co-ordinated *via* Ag–C(methine) interactions and that the water molecule exhibits intermolecular hydrogen bonding. Sublimation studies showed that these compounds exhibit low volatilities and low thermal stability. The high degree of aggregation observed in the solid state probably explains their low volatility. As a result these species are unsuitable for the CVD of Ag using conventional precursor-delivery methods.

Table 5 Atomic coordinates (× 10^4)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
$[\mathrm{Ag(hfacac)(C_4H_8OS)_2}]$							
Ag	1 025(1)	8 892(1)	4 177(1)	C(10)	2 843(10)	8 470(8)	6 870(7)
S(1)	−1 969(2)	8 132(2)	3 439(2)	C(11)	1 565(10)	6 954(8)	6 136(8)
S(2)	3 519(2)	9 191(2)	5 737(2)	C(12)	2 394(10)	6 333(8)	4 362(8)
O(1)	1 439(8)	10 692(5)	3 304(5)	C(13)	3 812(9)	7 741(8)	4 755(9)
O(2)	1 682(7)	8 071(5)	2 255(5)	F(1)	2 780(19)	12 369(13)	1 346(12)
O(3)	−3 667(6)	4 987(5)	1 224(5)	F(2)	538(15)	11 979(14)	1 814(15)
O(4)	2 083(7)	6 060(5)	5 412(6)	F(3)	2 950(17)	13 275(13)	3 282(13)
C(1)	1 894(8)	10 786(7)	2 367(6)	F(4)	3 279(16)	7 060(14)	1 050(11)
C(2)	2 234(9)	9 867(7)	1 494(6)	F(5)	3 857(16)	8 483(12)	259(13)
C(3)	2 134(8)	8 619(8)	1 523(6)	F(6)	1 397(16)	6 823(14)	−616(13)
C(4)	2 050(11)	12 088(9)	2 197(8)	F(1b)	1 901(19)	11 997(13)	987(12)
C(5)	2 582(11)	7 746(11)	507(9)	F(2b)	3 580(17)	13 307(14)	3 263(13)
C(6)	−2 676(10)	7 432(8)	1 624(8)	F(3b)	989(16)	12 502(14)	2 484(15)
C(7)	−2 608(10)	6 122(9)	999(7)	F(4b)	3 908(18)	7 801(16)	1 041(13)
C(8)	−3 045(10)	5 281(8)	2 581(8)	F(5b)	3 006(18)	8 362(13)	−353(14)
C(9)	−3 166(10)	6 498(9)	3 487(8)	F(6b)	1 208(17)	6 392(15)	−316(14)
$[\{\mathrm{Ag(hfacac)}\}_2\mathrm{(nbd)}]$							
Ag(1)	471(1)	3 604(1)	4 399(1)	C(7)	−1 647(9)	1 313(8)	1 282(7)
O(1)	2 197(6)	5 138(5)	6 288(5)	C(8)	−2 535(9)	1 301(8)	2 167(7)
C(1)	2 092(9)	5 058(7)	7 341(7)	O(4)	−2 230(6)	2 130(5)	3 214(5)
C(2)	732(9)	4 507(8)	7 722(7)	C(9)	687(11)	2 117(10)	362(8)
C(3)	−789(9)	3 981(7)	7 006(7)	F(7)	1 907(8)	1 756(7)	633(6)
O(2)	−1 250(6)	3 903(5)	5 896(4)	F(8)	−205(8)	1 259(7)	−688(5)
C(4)	3 675(10)	5 662(10)	8 302(8)	F(9)	1 311(10)	3 203(7)	164(6)
F(1)	4 771(14)	5 221(11)	7 886(10)	C(10)	−4 077(10)	139(9)	1 866(8)
F(2)	4 346(13)	6 940(10)	8 472(10)	F(10)	−4 393(8)	−765(6)	822(6)
F(3)	3 644(12)	5 604(11)	9 408(10)	F(11)	−5 334(7)	476(7)	1 791(8)
F(1′)	3 860(19)	4 748(16)	8 802(14)	F(12)	−4 125(12)	−328(9)	2 748(8)
F(2′)	3 656(19)	6 482(17)	9 302(15)	Ag(2)	−3 732(1)	2 986(1)	4 418(1)
F(3′)	4 926(20)	5 876(16)	7 802(15)	C(11)	−6 045(9)	3 144(8)	5 067(8)
C(5)	−2 142(10)	3 364(10)	7 578(8)	C(12)	−6 518(9)	2 512(8)	3 846(8)
F(4)	−1 722(7)	3 560(10)	8 743(6)	C(13)	−7 577(9)	1 125(8)	3 642(8)
F(5)	−3 283(7)	3 852(8)	7 473(7)	C(14)	−9 078(9)	1 208(8)	4 095(9)
F(6)	−2 882(11)	2 138(7)	6 962(9)	C(15)	−8 632(10)	1 829(8)	5 301(9)
O(3)	653(6)	3 223(5)	2 369(5)	C(16)	−6 807(10)	2 164(8)	5 695(8)
C(6)	−156(9)	2 266(8)	1 442(7)	C(17)	−6 754(10)	920(8)	4 797(8)
$[\{\mathrm{Ag(hfacac)}\}_2\mathrm{(H_2O)}]$							
Ag(1)	1 295(1)	983(1)	2 100(1)	C(10)	960(7)	−3 113(7)	−938(7)
Ag(2)	−2 591(1)	−460(1)	3 077(1)	F(1)	−48(7)	3 647(6)	5 395(6)
O(1)	361(4)	1 229(4)	4 049(3)	F(2)	−993(5)	1 653(5)	6 035(5)
O(2)	3 633(4)	1 587(5)	3 984(4)	F(3)	1 249(6)	3 466(6)	7 328(4)
O(3)	−1 515(4)	−973(4)	1 264(4)	F(4)	6 262(5)	3 547(6)	7 275(5)
O(4)	1 439(4)	−1 206(4)	930(4)	F(5)	6 354(6)	4 711(7)	5 781(8)
C(1)	1 253(6)	2 095(6)	5 214(5)	F(6)	6 709(6)	2 757(9)	5 540(7)
C(2)	2 951(7)	2 599(6)	5 852(5)	F(7)	−4 667(5)	−3 331(5)	492(4)
C(3)	4 002(6)	2 386(6)	5 154(5)	F(8)	−4 722(5)	−3 707(6)	−1 596(4)
C(4)	371(7)	2 740(7)	6 012(6)	F(9)	−4 504(5)	−1 623(5)	−534(7)
C(5)	5 852(7)	3 355(8)	5 923(7)	F(10)	1 898(8)	−3 531(8)	−213(6)
C(6)	−2 139(6)	−1 996(6)	165(5)	F(11)	1 862(9)	−2 262(7)	−1 590(7)
C(7)	−1 360(6)	−2 579(6)	−579(5)	F(12)	−188(6)	−4 237(7)	−1 915(7)
C(8)	356(6)	−2 192(6)	−88(5)	O(5)	−4 870(6)	−80(6)	2 736(5)
C(9)	−4 030(6)	−2 681(7)	−392(6)				

Acknowledgements

M. J. H.-S. and T. T. K. thank the National Science Foundation (NSF) (No. CHE-9107035) for funding this work. M. J. H.-S. thanks the NSF chemical instrumentation program for purchase of a low-field NMR spectrometer and the Air Force Office of Scientific Research and the Dreyfus Foundation for the purchase of an X-ray powder diffractometer.

References

1 A. Zinn, B. Neimer and H. D. Kaesz, *Angew. Chem., Adv. Mater.*, 1992, **4**, 375.

2 T. Mayer, *Mater. Res. Soc. Bull.*, 1993, **18**.

3 T. H. Baum and P. Comita, in *The Chemistry of Metal CVD*, eds. T. T. Kodas and M. J. Hampden-Smith, VCH, Weinheim, 1994, ch. 6.

4 M. J. Hampden-Smith and T. T. Kodas, in *The Chemistry of Metal CVD*, eds. T. T. Kodas and M. J. Hampden-Smith, VCH, Weinheim, 1994, ch. 5.

5 A. Maverick and G. L. Griffin, in *The Chemistry of Metal CVD*, eds. T. T. Kodas and M. J. Hampden-Smith, VCH, Weinheim, 1994, ch. 4.

6 Z. Y. Li, H. Maeda, K. Kusakabe, S. Morooka, H. Anzai and S. Akiyama, *J. Membrane Sci.*, 1993, **78**, 247.

7 J. Shu, B. P. A. Grandjean, A. Van Neste and S. Kalaiguine, *Can. J. Chem. Eng.*, 1991, **69**, 1036.

8 D. Wu, R. A. Outlaw and R. L. Ash, *J. Appl Phys.*, 1993, **74**, 4990.

9 R. Jaraith, A. Jain, R. D. Tolles, M. J. Hampden-Smith and

T. T. Kodas, in *The Chemistry of Metal CVD*, eds. T. T. Kodas and M. J. Hampden-Smith, VCH, Weinheim, 1994, ch. 1.

10 A. Jain, K.-M. Chi, M. J. Hampden-Smith, T. T. Kodas, M. F. Paffett and J. D. Farr, *Chem. Mater.*, 1991, **3** 995.

11 A. Jain, K.-M. Chi, M. J. Hampden-Smith, T. T. Kodas, M. F. Paffett and J. D. Farr, *J. Mater. Res.*, 1992, **7**, 261.

12 A. Jain, K.-M. Chi, M. J. Hampden-Smith, T. T. Kodas, M. F. Paffett and J. D. Farr, *J. Electrochem. Soc.*, 1993, **140**, 1434.

13 P. M. Jefferies, L. H. Dubois and G. S. Girolami, *Chem. Mater.*, 1992, **4**, 1169.

14 R. Kumar, F. R. Fronczek, A. W. Maverick, G. W. Lai and G. L. Griffin, *Chem. Mater.*, 1992, **4**, 577.

15 J. A. T. Norman, B. A. Muratore, P. N. Dyer, D. A. Roberts and A. K. Hochberg, *J. Phys. (Paris)*, 1992, **4**, C2.

16 J. A. T. Norman, D. A. Roberts and A. K. Hochberg, *Mater. Res. Soc. Symp. Proc.*, 1993, **282**, 347.

17 S. L. Cohen, M. Liehr and S. Kasi, *Appl. Phys. Lett.*, 1992, **60**, 50.

18 N. Awaya and Y. Arita, in *Advanced Metallization for ULSI Applications*, Materials Research Society, Pittsburgh, PA, 1991, vol. 5, p. 231.

19 Y. Chang, *Mater. Res. Soc. Symp. Proc.*, 1993, **282**, 335.

20 A. E. Kaloyeros, A. Feng, J. Garhart, K. C. Brooks, S. K. Gosh, A. N. Saxena and F. Luethers, *J. Electronic Mater.*, 1990, **19**, 271.

21 W. Rees, in *Mater. Res. Soc. Symp. Proc.*, 1992, **250**, 297.

22 P. F. Seidler, S. P. Kowalczyk, M. M. Banaszak, J. J. Yurkas, M. H. Norcott and F. R. McFeely, *Mater. Res. Soc. Symp. Proc.*, 1993, **282**, 359.

23 T. T. Kodas and P. B. Comita, *J. Appl. Phys.*, 1988, **65**, 2413.

24 T. T. Kodas and P. B. Comita, *Acc. Chem. Res.*, 1990, **23**, 188.

25 P. M. Jeffries, S. R. Wilson and G. S. Girolami, *J. Organomet. Chem.*, 1993, **449**, 203.

26 C. Oehr and H. Suhr, *Appl. Phys. A*, 1989, **49**, 691.

27 D. B. Beach and J. M. Jasinski, *US Pat.*, 4 948 623, 1990.

28 M. J. Shapiro, W. J. Lackey, J. A. Hanigofsky, D. N. Hill, W. B. Carter and E. K. Barefield, *J. Alloys Compounds*, 1992, **187**, 331.

29 N. H. Dryden, J. J. Vittal and R. J. Puddephatt, *Chem. Mater.*, 1993, **5**, 765.

30 W. Lin, T. H. Warren, R. G. Nuzzo and G. S. Girolami, *J. Am. Chem. Soc.*, 1993, **115**, 11644.

31 T. H. Baum, C. E. Larson and G. May, *J. Organomet. Chem.*, 1992, **425**, 189.

32 T. H. Baum and C. E. Larson, *Chem. Mater.*, 1992, **4**, 365.

33 T. H. Baum and C. E. Larson, *J. Electrochem. Soc.*, 1993, **140**, 154.

34 K.-M. Chi, H. K. Shin, M. J. Hampden-Smith, T. T. Kodas and E. N. Duesler, *Polyhedron*, 1991, **10**, 2293.

35 K.-M. Chi, H. K. Shin, M. J. Hampden-Smith, T. T. Kodas and E. N. Duesler, *Inorg. Chem.*, 1991, **30**, 4293.

36 H.-K. Shin, M. J. Hampden-Smith, T. T. Kodas and E. N. Duesler, *Can. J. Chem.*, 1992, **70**, 2954.

37 H. K. Shin, K. M. Chi, J. Farkas, M. J. Hampden-Smith, T. T. Kodas and E. N. Duesler, *Inorg. Chem.*, 1992, **31**, 424.

38 A. Bailey, T. S. Corbitt, M. J. Hampden-Smith, E. N. Duesler and T. T. Kodas, *Polyhedron*, 1993, **12**, 1785.

39 C. Roger, T. S. Corbitt, M. J. Hampden-Smith and T. T. Kodas, *Appl. Phys. Lett.*, submitted.

40 J. Farkas, M. J. Hampden-Smith and T. T. Kodas, *J. Phys. Chem.*, 1994, **98**, 6753, 6763.

41 F. D. Hardcastle, J. Farkas, C. H. F. Peden, T. R. Omstead, R. S. Blewer, M. J. Hampden-Smith and T. T. Kodas, in *Advanced Metallization for ULSI Applications*, eds. V. S. Rana and R. V. Joshi, Materials Research Society, Pittsburgh, PA, 1992, p. 413.

42 G. Doyle, K. A. Eriksen and D. Van Engen, *Organometallics*, 1985, **4**, 830.

43 G. M. Sheldrick, SHELXTL PLUS, Siemens Analytical Instruments Inc., Madison, WI, 1990.

44 H. Gunther, in *NMR Spectroscopy, An Introduction*, Wiley, New York, 1980, p. 243.

45 K. Nakamoto, in *Infrared and Raman Spectra of Inorganic and Co-ordination Compounds*, Wiley, New York, 1986, p. 259.

46 C. K. Johnson, ORTEP, Report ORNL-5138, Oak Ridge National Laboratory, Oak Ridge, TN, 1976.

47 N. C. Baenziger, H. L. Haight and J. R. Doyle, *Inorg. Chem.*, 1964, **3**, 1535.

48 D. R. Lide, in *CRC Handbook of Chemistry and Physics*, 74th edn, CRC Press, Boca Raton, FL, 1993–1994, pp. 9–25.

49 J. A. Dean, in *Lange's Handbook of Chemistry*, 14th edn, McGraw-Hill, New York, 1992, Sect. 4.

50 A. G. Swallow and M. R. Truter, *Proc. R. Soc. London, Ser. A*, 1962, **266**, 527.

51 A. Robson and M. R. Truter, *J. Chem. Soc.*, 1965, 630.

52 A. G. Swallow and M. R. Truter, *Proc. R. Soc. London, Ser. A*, 1960, 254.

53 A. C. Hazell and M. R. Truter, *Proc. R. Soc. London, Ser. A*, 1960, 218, 254.

54 J. Fornies, R. Navarro, M. Tomas and E. P. Urriolabettia, *Organometallics*, 1993, **12**, 940.

55 W. H. Watson and C.-T. Lin, *Inorg. Chem.*, 1966, **5**, 1074.

Received 27th April 1994; Paper 4/02521K