Antimony β-diketonates and alkoxide/β-diketonates: remarkable formation of a 3,4-dihydro-2*H*-pyran ring by coupling of 1,1,1,5,5,5-hexafluoro-2,4-pentanedione ligands

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Homoleptic antimony(III) β-diketonates Sb(thd)$_3$ (Hthd = 2,2,6,6-tetramethyl-3,5-heptanedione) and Sb(fod)$_3$ (Hfod = 2,2-dimethyl-6,6,7,7,8,8,8-heptafluoro-3,5-heptanedione) have been synthesised from Sb(OEt)$_3$ and three equivalents of the appropriate ligand. Both compounds have been characterised crystallographically and are monomeric with pseudo seven-coordination at antimony, where each ligand chelates the metal in an anisobidentate manner. Attempts to prepare Sb(hfac)$_3$ (Hhfac = 1,1,1,5,5,5-hexafluoro-2,4-pentanedione) by the same route generated a compound of formula [(EtO)Sb(hfac)$_2$]$_2$ but in which the two β-diketonate ligands have combined to produce a functionalised 3,4-dihydro-2*H*-pyran ring; the dimer arises from a bridging ethoxy group. Heteroleptic (EtO)Sb(thd)$_2$ has also been synthesised and crystallographically characterised as a monomeric structure in which the ethoxy group is terminal. In addition, Sb(OEt)$_2$(fod) and Sb(OEt)$_4$(thd) have been prepared for comparison.

Introduction

Our interest in the chemistry of antimony oxide-based sensors and the chemical vapour deposition (CVD) of such materials[1,2] has caused us to focus our attention on the synthesis of precursors for these procedures. In this regard, we have recently reported on the chemistry of monomeric antimony alkoxides[3] and carbamates,[4] the latter in particular proving to be excellent CVD precursors. Other classes of compound which are widely exploited in the CVD of oxide films are homoleptic metal β-diketonates, M(β-dk)$_n$, and the heteroleptic complexes which also incorporate alkoxide ligands, M(β-dk)$_n$(OR)$_m$.[5,6]

Surprisingly, despite the widespread study of β-diketonates of most elements in the Periodic Table,[7–9] almost nothing is known about the antimony species Sb(β-dk)$_3$ or related Sb(β-dk)$_n$(OR)$_{3-n}$. A review cites the NMR data for *inter alia* Sb(hfac)$_3$, Sb(fod)$_3$ and Sb(thd)$_3$, though the data appear to be contained in a thesis and have not reached the primary literature,[10] along with two old references for the synthesis of Sb-(β-dk)$_3$.[11,12] To our knowledge, no structural studies have previously been carried out. There have been more substantial studies of Sb(v) β-diketonates, including Sb(acac)Cl$_4$,[13,14] Ph$_2$Sb-(acac)Cl$_2$,[15] Ph$_3$Sb(β-dk)$_2$ and Ph$_3$Sb(OMe)(β-dk)$_3$.[16]

In this report we detail the synthesis and structural characterisation of representative members of each of these two compound classes and the unprecedented coupling of β-diketonate ligands on a metal centre to form a functionalised 3,4-dihydro-2*H*-pyran ring.

Experimental

General procedures

Elemental analyses were performed using an Exeter Analytical CE 440 analyser. In certain cases *e.g.* **1**, **2**, **5**, difficulty was experienced in obtaining accurate microanalysis data as the compounds readily decomposed on weighing. The composition and purity of these species has been established by NMR and X-ray crystallography. NMR spectra were recorded at room temperature on a Bruker Avance 300 MHz FT-NMR (¹H, ¹³C) or Varian Mercury 400BB spectrometer operating at 376 MHz (¹⁹F), using saturated solutions in either CDCl$_3$, *d*⁶-benzene or *d*⁸-THF.

All β-diketones were obtained from commercial sources and used as supplied. Sb(OEt)$_3$ and Sb(OEt)$_5$·NH$_3$ were prepared by published procedures.[3,17] Hexane and toluene were distilled over CaH$_2$ prior to use. All reactions were carried out in an inert atmosphere (N$_2$ and Ar) using a dry-box and Schlenk-line techniques. Melting points were recorded in sealed glass capillary tubes with a Gallenkamp melting point apparatus. Thermogravimetric studies were performed on a Perkin-Elmer TGA7 analyser; samples were loaded as quickly as possible in air then the temperature increased under a flow of dry N$_2$ gas; the heating rate was 20 deg min⁻¹.

Synthesis of Sb(thd)$_3$ (1). Antimony(III) ethoxide (2.36 g, 9.19 mmol) was diluted in dry toluene (20 ml). To this solution 2,2,6,6-tetramethyl-3,5-heptanedione (Hthd, 5.74 ml, 27.50 mmol) was added in a dropwise manner. The mixture was then stirred at room temperature for 24 hours and the volatiles removed *in vacuo* to yield a tacky white solid. The product was stirred in dry hexane (10 ml) for 15 min, and again dried at reduced pressure. The product, now a white polycrystalline powder, was dissolved in toluene (15 ml) and placed in a freezer. Colourless, air-sensitive crystals were obtained overnight (yield 4.84 g, 78%; mp 80–82 °C). Analysis, found (calc. for C$_{33}$H$_{57}$O$_6$Sb): C: 57.6 (59.0); H: 7.44 (8.56)%. ¹H NMR (270 MHz, C$_6$D$_6$, δ): 1.17 (s, 54H, CH$_3$), 5.77 (s, 3H, CH). ¹³C NMR (68 MHz, C$_6$D$_6$, δ): 28.5 (CH$_3$), 41.6 (*C*CH$_3$), 91.6 (CH), 195.9 (CO).

Synthesis of Sb(fod)$_3$ (2). Antimony(III) ethoxide (0.99 g, 3.86 mmol) was diluted in dry hexane (20 ml). While stirring at room temperature, 2,2-dimethyl-6,6,7,7,8,8,8-heptafluoro-3,5-

heptanedione (Hfod, 2.68 ml, 11.59 mmol) was slowly added *via* a syringe. As the β-diketone was added, the solution became slightly yellow in colour. The mixture was stirred for one hour, then the volatiles were removed *in vacuo*, yielding a white poly-crystalline solid, which was dissolved in toluene (10 ml) and placed in a freezer. Overnight, colourless crystals were obtained (yield 3.32 g, 85%; mp 94 °C). ^{1}H NMR (400 MHz, CDCl$_3$, δ): 1.27 (s, 27H, CH$_3$), 6.13 (s, 3H, CH). ^{13}C NMR (100 MHz, CDCl$_3$, δ): 25.4 (CH$_3$), 41.5 (*C*CH$_3$), 94.9 (CH), 107.3 (CF$_2$, ^1J = 260 Hz, ^2J = 32 Hz), 109.9 (CF$_2$, ^1J = 260 Hz, ^2J = 32 Hz), 116.9 (CF$_3$, ^1J = 287 Hz, ^2J = 34 Hz), 165.9 (t, CF$_2$*C*O, J = 27 Hz), 206.5 (CO).

Attempted synthesis of Sb(hfac)$_3$ (3). Antimony(III) ethoxide (1.79 g, 6.97 mmol) was diluted in dry toluene (20 ml). While stirring at room temperature, 1,1,1,5,5,5-hexafluoro-2,4-pentanedione (Hhfac, 2.96 ml, 4.34 g, 20.90 mmol) was slowly added by syringe. On addition of the β-diketone, the solution became pale yellow in appearance. The mixture was stirred for 16 hours, and then all volatiles were removed *in vacuo*, yielding a creamy-white sticky material. Dry hexane (30 ml) was added to the flask, and the contents stirred for 10 min. On settling a white solid, clearly with poor solubility in hexane, was observed which was isolated by cannula filtration. The white solid was then dried at reduced pressure, and redissolved in warm toluene (30 ml) and placed in a freezer. Within hours, clear colour-less crystals were obtained (yield 2.88 g, 56%; mp 76–77 °C). Crystallography indicates that while the compound has the same empirical formula as Sb(OEt)(hfac)$_2$, the two β-diketon-ates have undergone a coupling to yield a functionalised 3,4-dihydro-2*H*-pyran ring. Analysis, found (calc. for C$_{12}$H$_7$F$_{12}$O$_5$Sb): C, 24.6 (24.8); H, 1.64 (1.22)%. ^{1}H NMR (400 MHz, d^8-THF, δ): 1.02 (t, 3H, CH$_3$, ^3J = 7 Hz), 1.62 (s, 1H, C^{4}H), 3.48 (q, 2H, CH$_2$, ^3J = 7 Hz), 5.08 (s, 1H, C^{2}H). ^{13}C NMR (100 MHz, CDCl$_3$, δ) 13.0 (CH$_3$), 40.9 (C^4), 56.1 (CH$_2$), 90.8 (br, C^3 or C^5), 92.2 (q, C^3 or C^5, ^2J = 32 Hz), 98.4 (C^2), 110–125 (complex, 4 CF$_3$), 145.4 (q, C^1, ^2J = 34 Hz), 172.5 (q, CO, ^2J = 36 Hz). ^{19}F NMR (376 MHz, d^8-THF, δ): −74.9, −76.7 br, −83.6 [3CF$_3$, C(O)CF$_3$].

Synthesis of Sb(OEt)(thd)$_2$ (4). Antimony(III) ethoxide (1.32 g, 5.14 mmol) was diluted in dry hexane (20 ml). While stirring at room temperature, Hthd (2.14 ml, 1.88 g, 10.27 mmol) was added *via* a syringe. The mixture was allowed to stir at room temperature for 18 hours, at which point the volatiles were removed *in vacuo*, yielding a clear viscous liquid. Hexane (5 ml) was added and the solution was placed in a freezer com-partment, where clear block-shaped crystals were obtained (Yield 1.90 g, 69%; mp 82 °C). Analysis, found (calc. for C$_{24}$H$_{43}$O$_5$Sb): C, 45.7 (45.6), H, 7.39 (7.40)%. ^{1}H NMR (270 MHz, C$_6$D$_6$, δ): 1.27 (s, 18H, CCH$_3$), 1.36 (t, 6H, CH$_3$, ^3J = 7.0 Hz), 4.19 (q, 4H, CH$_2$, ^3J = 6.9 Hz), 5.94 (s, 1H, C–H). ^{13}C NMR (68 MHz, C$_6$D$_6$, δ): 20.6 (CH$_3$), 28.6 (CH$_3$), 42.0 (*C*CH$_3$), 59.4 (CH$_2$), 92.8 (CH), 198.3 (CO).

Synthesis of Sb(OEt)$_2$(fod) (5). Antimony(III) ethoxide (1.39 g, 5.37 mmol) was diluted in dry hexane (20 ml). While stirring at room temperature, Hfod (1.24 ml, 5.37 mmol) was added *via* a syringe; while there was no clear reaction, a slight yellow colouration developed. The mixture was allowed to stir at room temperature overnight, at which point the volatiles were removed *in vacuo*, yielding a slightly yellow viscous liquid. Analysis, found (calc. for C$_{14}$H$_{20}$F$_7$O$_4$Sb): C, 32.5 (33.37); H, 3.52 (3.98)%. ^{1}H NMR (400 MHz, C$_6$D$_6$, δ): 0.93 (s, 27H, CH$_3$C), 1.18 (t, 6H, CH$_3$CH$_2$, ^3J = 7 Hz), 3.99 (q, 4H, CH$_3$C*H*$_2$, ^3J = 7 Hz), 6.11 (s, 1H, CH). ^{13}C NMR (100 MHz, C$_6$D$_6$, δ): 18.2 (*C*H$_3$CH$_2$), 25.4 (*C*H$_3$C), 41.5 (CH$_3$*C*), 58.0 (CH$_2$), 94.9 (CH), 105–110 (complex, CF$_2$CF$_2$), 116.9 (qt, CF$_3$, $^{1,2}J$ = 286, 34 Hz), 163.8 (t, CF$_2$*C*O, ^2J = 24 Hz), 204.8 (CO). ^{19}F NMR (376 MHz, d^8-THF, δ): −81.4 (CF$_3$), −119.5 (CCF$_2$), −126.9 (C*F*$_2$CF$_3$).

Synthesis of Sb(OEt)$_4$(thd) (6). Sb(OEt)$_5$·NH$_3$[3] (0.70 g, 1.93 mmol) was dissolved in dry toluene (15 ml), brought to reflux and Hthd (0.39 ml, 1.80 mmol) was added. Reflux was con-tinued for 1 h after which time volatiles were removed *in vacuo*. The viscous liquid which remained (6) was pure by NMR. ^{1}H NMR (400 MHz, C$_6$D$_6$, δ): 0.81 (s, 18H, CH$_3$C), 0.99 (t, 6H, CH$_3$CH$_2$, ^3J = 7 Hz), 1.17 (t, 6H, CH$_3$CH$_2$, ^3J = 7 Hz), 3.85 (q, 4H, CH$_3$C*H*$_2$, ^3J = 7 Hz), 4.14 (q, 4H, CH$_3$C*H*$_2$, ^3J = 7 Hz), 5.58 (s, 1H, CH). ^{13}C NMR (100 MHz, C$_6$D$_6$, δ): 17.7 (*C*H$_3$CH$_2$), 17.9 (*C*H$_3$CH$_2$), 26.4 (*C*H$_3$C), 40.6 (CH$_3$*C*), 59.4 (CH$_2$), 59.8 (CH$_2$), 91.5 (CH), 203.0 (CO).

Crystal structures

Experimental details relating to the single-crystal X-ray crystal-lographic study of complexes **1**–**4** are given in Table 1. Data were collected on either an Enraf Nonius CAD 4 (**1**) or a Non-ius Kappa CCD diffractometer (**2**–**4**) at 170 K, save that for **3** which was collected at 150 K. The refinement method was full-matrix least-squares on F^2. In the cases of **2**–**4** a semi-empirical absorption correction from equivalents was made. Hydrogen atoms were included at calculated positions. For **4** there is dis-order (3 : 2) in methyl groups based on C(16)–C(18) of which only the major component is shown in Fig. 5. Software used: SHELXS 86,[18] SHELXL 97,[19] ORTEX.[20]

CCDC reference numbers 191922–191925.

See http://www.rsc.org/suppdata/dt/b2/b208110e/ for crystal-lographic data in CIF or other electronic format.

Results and discussion

Synthetic aspects

Antimony(III) β-diketonates based on 2,2,6,6-tetramethyl-3,5-heptanedione (thd, **1**) and 2,2-dimethyl-6,6,7,7,8,8,8-hepta-fluoro-3,5-heptanedione (fod, **2**) have been straightforwardly prepared by the reaction of Sb(OEt)$_3$ and the corresponding β-diketonate ligand in toluene/hexane. Yields are *ca.* 80%.

R^1 = R^2 = ^{t}Bu (**1**)
R^1 = ^{t}Bu, R^2 = C$_3$F$_7$ (**2**)
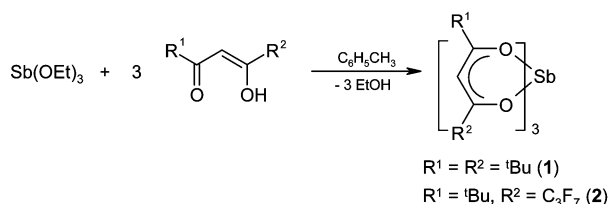
The compounds are air-sensitive, crystalline solids which are soluble in common organic solvents. They have reasonably low melting points (<95 °C) and, in the light of the simplicity of their NMR spectra which show only one ligand environment, adopt symmetrical structures. Both **1** and **2** are volatile and begin to lose weight even at room temperature, though this initial weight loss is likely to be due to aerial hydrolysis which has made obtaining accurate microanalysis data a problem. The TGA of **2** (Fig. 1), recorded under an N$_2$ atmosphere, shows a continuous but two-stage weight loss from room temperature up to *ca.* 200 °C, where the residual weight remaining (15.5%) is consistent with the formation of Sb$_2$O$_3$ (theoretical: 14.4%) though we have not analysed the residue further. Unfortunately, preliminary atmospheric-pressure chemical vapour deposition (CVD) experiments using Sb(thd)$_3$ (**1**) (bubbler temperature: 150 °C, glass substrate: 500 °C) or aerosol-assisted CVD using either **2** or **3** in THF (glass substrate temperatures 400 and 500 °C, respectively) have proved unsuccessful in depositing either Sb(0) or antimony oxide films, in contrast to our successful deployment of antimony alkoxides[1,2] and carbamates[4] in this area.

In contrast, the attempted preparation of Sb(hfac)$_3$ by the same route resulted in a compound (**3**) of low solubility (save

Table 1 Crystallographic data for **1**–**4**

	1	2	3	4
Empirical formula	$C_{33}H_{57}O_6Sb$	$C_{30}H_{30}F_{21}O_6Sb$	$C_{12}H_7F_{12}O_5Sb$	$C_{24}H_{43}O_5Sb$
Formula weight	671.54	1007.29	580.93	533.33
Crystal system	Triclinic	Cubic	Triclinic	Monoclinic
Space group	$P\bar{1}$	$Pa\bar{3}$ (no. 205)	$P\bar{1}$	$C2/c$
a/Å	10.146(3)	19.8180(3)	8.3580(3)	26.4980(5)
b/Å	13.272(3)	19.8180(3)	9.9790(3)	11.7800(2)
c/Å	14.361(4)	19.8180(3)	12.0670(4)	18.3430(3)
a/°	77.86(2)		66.205(1)	
β/°	69.81(2)		87.485(1)	107.583(1)
γ/°	78.49(2)		70.417(1)	
Volume/Å^3	1757.3(8)	7783.6(2)	862.74(5)	5458.2(2)
Z	2	8	2	8
μ(Mo-Kα)/mm^{-1}	0.823	0.849	1.749	1.038
Independent reflections	6166 [R(int) = 0.0142]	2642 [R(int) = 0.0894]	3919 [R(int) = 0.0587]	7957 [R(int) = 0.0524]
Goodness-of-fit on F^2	0.656	1.018	1.077	0.755
Final R_1, wR_2 [$I > 2\sigma(I)$]	0.0315, 0.1124	0.0452, 0.1046	0.0392, 0.0932	0.0353, 0.1011
Final R_1, wR_2 (all data)	0.0400, 0.1261	0.0646, 0.1151	0.0476, 0.0976	0.0558, 0.1219
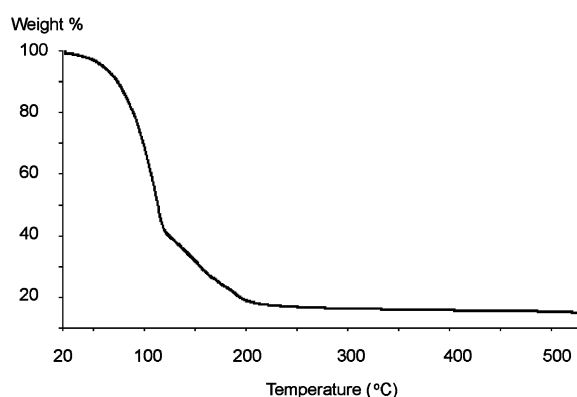
Fig. 1 TGA of **2**.

for THF) which microanalysis indicates has an empirical formula corresponding to (EtO)Sb(hfac)$_2$. However, the ^{13}C NMR of **3** is too complex for such a species and crystallography has shown that the two hfac ligands have combined to form the 3,4-dihydro-2H-pyran product (shown schematically below, along with the NMR numbering):


(3)
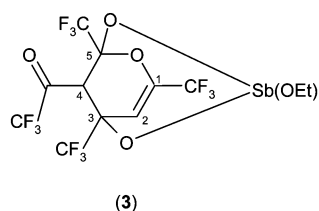
A claim has previously been made for the synthesis of Sb(hfac)$_3$, unsubstantiated by spectral or structural data, and which has a very similar melting point (74–76 °C)[10] to **3** (76–77 °C).

In the ^{1}H NMR spectrum, singlets due to the protons attached to C^4 (1.62 ppm) and C^2 (5.08 ppm) are visible in addition to the triplet and quartet of the ethoxide group. In the ^{13}C NMR spectrum, C^4 appears at 40.9 ppm, between the signals for the carbons of the ethoxide (13.0, 56.1 ppm) while the singlet at 98.4 can be assigned to the other olefinic carbon, C^2. Three carbons experiencing ^2J coupling to the CF$_3$ groups are identified as quartets with coupling constants of *ca.* 35 Hz (C^1 145.4 ppm, ^2J 34 Hz; CO 172.5 ppm, J 36 Hz; C^3 or C^5 92.2 ppm, J 32 Hz) along with a broad resonance at 90.8 ppm (C^3 or C^5). The CF$_3$ groups are less easy to resolve and give rise to a complex pattern of signals in the range 110–125 ppm. However, these four groups are visible in the ^{19}F NMR spectrum, as singlets at −74.9, −76.7 and −83.6 ppm, the central signal

being rather broad and presumably reflecting two overlapping resonances.

The mechanism of formation of **3** is intriguing. Known syntheses of dihydro-2H-pyrans in which formation of at least two bonds is required (*i.e.* not a ring closure reaction or the transformation of a pre-formed heterocycle) generally involve hetero Diels–Alder reactions.[21,22] However, it has been noted that the dimerisation of an α,β-unsaturated carbonyl is a difficult reaction and the reaction of, for example, propenal with alkenes only takes place at >180 °C under pressure to give low yields of product.[23] Vinyl ethers are more reactive dienophiles but are not present in the reaction to produce **3**.[24] We therefore propose the mechanism shown in Scheme 1.
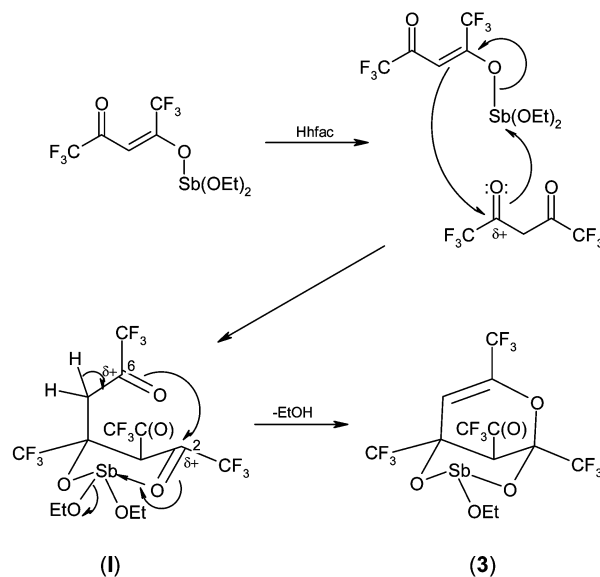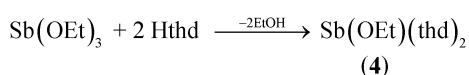

Scheme 1

After initial substitution of one ethoxy group of Sb(OEt)$_3$ by hfac, a second β-diketonate coordinates the antimony through its carbonyl oxygen and C–C bond formation occurs to afford intermediate (**I**). We propose that (**I**) is formed because of (i) the formation of a stable six-membered ring, (ii) the electrophilic nature of the carbonyl that has an α-CF$_3$ substituent and (iii) the low pK_a of hfac which promotes enolisation. Intramolecular ring closure then occurs to generate the 3,4-dihydro-2H-pyran (**3**) which is promoted by the proximity of the C$_6$ carbonyl group to the second electrophilic C$_2$ carbonyl moiety.

As this reaction only occurs with the hfac ligand and not thd or fod, it would seem reasonable that the two electron withdrawing CF$_3$ groups are required both to enhance the electro-

philic character of the carbonyl groups to nucleophilic attack and stabilise the carbanionic character of the central carbon atom. Indeed, the intramolecular reaction of water and tfac [$CF_3C(O)CHC(O)CH_3$], both simultaneously coordinated to a triphenylantimony, to yield $Ph_3Sb[CF_3C(O)_2CH_2C(O)CH_3]$ has been reported, with attack at the more electrophilic $C(O)CF_3$ centre. However, the reaction is only observed when fluorinated β-diketonates are involved.[25] Nonetheless, what is puzzling is why the dimerisation reaction is mediated by antimony alone, since numerous other metal bis- and tris-hfac complexes are known where this coupling reaction does not occur.[26–29] This reaction may offer some scope for the synthesis of other dihydro-2H-pyran rings, by initial addition of one equivalent of Hhfac followed by a second equivalent of a different β-diketonate.

Heteroleptic β-diketonate/alkoxide complexes, a combination frequently used to tailor the volatility of CVD precursors,[6,30,31] can be prepared by stoichiometric addition of β-diketonate to $Sb(OEt)_3$:

$$Sb(OEt)_3 + 2\ Hthd \xrightarrow{-2EtOH} Sb(OEt)(thd)_2$$

$$(4)$$

$$Sb(OEt)_3 + Hfod \xrightarrow{-EtOH} Sb(OEt)_2(fod)$$

$$(5)$$

Compound **4** is a crystalline solid while **5** is a viscous, yellowish oil. The NMR spectra of both compounds are simple, which suggest monomeric structures in both cases, a feature confirmed in the crystallographic analysis of **4**.

For comparison we have also synthesised a heteroleptic Sb(v) analogue, by the stoichiometric addition of Hthd to $Sb(OEt)_5 \cdot NH_3$.[3]

$$(6)$$
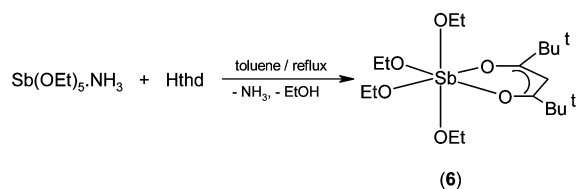
After removal of volatiles, **6** remains as an oil. The NMR of **6** shows it to be pure, while the two environments for the ethoxy groups are clearly visible in 1 : 1 ratio in both the [1]H (triplets at 0.99 and 1.17 ppm; quartets at 3.85 and 4.14 ppm) and ^{13}C NMR spectra (CH_3: 17.7, 17.9; CH_2: 59.4, 59.8 ppm) establishing octahedral coordination about antimony.

Structural studies

The structures of the two antimony(III) β-diketonates **1** and **2** are shown in Figs. 2 and 3, respectively, along with selected metrical data in the figure captions. Both structures are similar, in that the antimony adopts a pseudo-seven coordinate geometry with three bidentate ligands in addition to the lone pair inherent on the metal. Each ligand binds to antimony in an anisobidentate manner, with one short [**1**: 2.055(3), 2.064(3), 2.065(3); **2**: 2.064(2) Å] and one long Sb–O bond [**1**: 2.446(3), 2.456(3), 2.468(3); **2**: 2.441(3) Å]. The C–O and C=O moieties within the β-diketonate are discernable, the former being *ca.* 0.38 Å longer than the latter in each of the two structures. The oxygens of each long Sb–O bond occupy an opened triangular face of the octahedron of oxygens about antimony, presumably to accommodate the lone electron pair on the metal. In related M(β-dk)₃ it should be noted that asymmetric coordination can occur even in the absence of lone pairs, though the difference in M–O bonds is usually less marked than in the cases of **1** and **2** *e.g.* Rh(acac)₃, (Rh–O: 1.962, 2.045 Å),[32] Al(acac)₃ (Al–O:
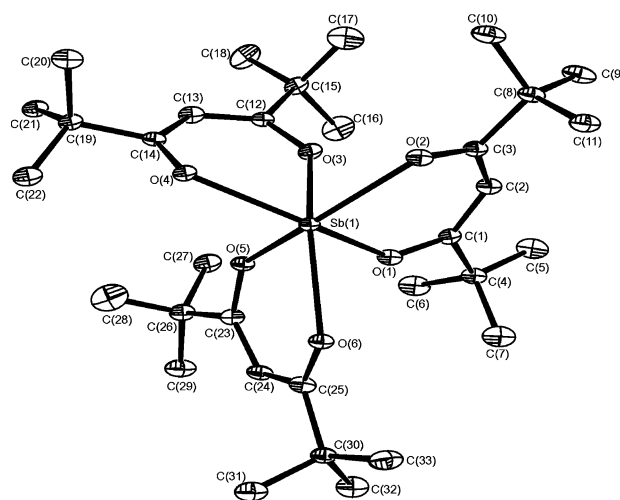
Fig. 2 The structure of **1** showing the asymmetric unit and the labelling scheme. Ellipsoids are at the 30% probability level. Selected metrical data: Sb(1)–O(1) 2.065(3), Sb(1)–O(2) 2.446(3), Sb(1)–O(3) 2.055(3), Sb(1)–O(4) 2.468(3), Sb(1)–O(5) 2.064(3), Sb(1)–O(6) 2.456(3), O(1)–C(1) 1.307(5), O(2)–C(3) 1.260(5), O(3)–C(12) 1.306(5), O(4)–C(14), 1.249(5), O(5)–C(23) 1.297(5), O(6)–C(25) 1.235(5) Å; O(1)–Sb(1)–O(2) 76.97(10), O(1)–Sb(1)–O(3) 82.72(11) O(1)–Sb(1)–O(4) 150.97(10), O(1)–Sb(1)–O(5) 83.12(10), O(1)–Sb(1)–O(6) 73.51(10), O(2)–Sb(1)–O(3) 74.37(10), O(2)–Sb(1)–O(4) 115.70(9), O(2)–Sb(1)–O(5) 151.53(10), O(2)–Sb(1)–O(6) 115.58(9), O(3)–Sb(1)–O(4) 76.54(9), O(3)–Sb(1)–O(5) 83.17(11), O(3)–Sb(1)–O(6) 150.52(10), O(4)–Sb(1)–O(5) 74.52(9), O(4)–Sb(1)–O(6) 117.78(9), O(5)–Sb(1)–O(6) 77.00(10)°.
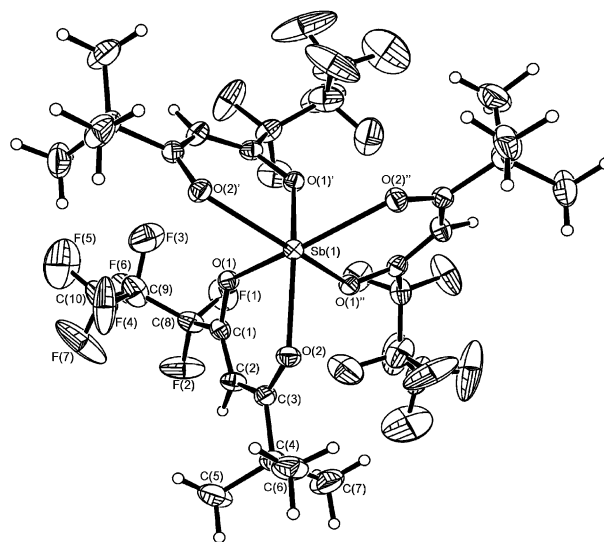
Fig. 3 The structure of **2** showing the asymmetric unit and the labelling scheme. Ellipsoids are at the 30% probability level. Selected metrical data: Sb(1)–O(1) 2.064(2), Sb(1)–O(2) 2.441(3), O(1)–C(1) 1.304(4), O(2)–C(3) 1.230(5) Å; O(1)–Sb(1)–O(1′) 82.63(11), O(1)–Sb(1)–O(2) 77.16(9), O(1′)–Sb(1)–O(2) 77.99(10), O(1)–Sb(1)–O(2′) 153.52(10), O(2)–Sb(1)–O(2′) 114.46(5)° (symmetry operation: *y*, *z*, *x*).

1.872, 1.899 Å).[33] In the case of **2**, the lone pair lies along the three-fold symmetry axis intrinsic in the structure and along which the molecular representation is viewed in Fig. 3.

Each short Sb–O bond is thus *trans* to a long bond of the same type. In the case of **2**, which involves an asymmetrically-substituted ligand, the C_3F_7 groups all lie on the same octahedral face and are associated with the short Sb–O bonds, while the ᵗBu groups are on the more open octahedral face.

Crystallographic analysis of **3** (Fig. 4) confirms the coupling of the two hfac ligands into a 3,4-dihydro-2H-pyran ring whose C=C double bond is evident between C(6) and C(7) [1.316(6)
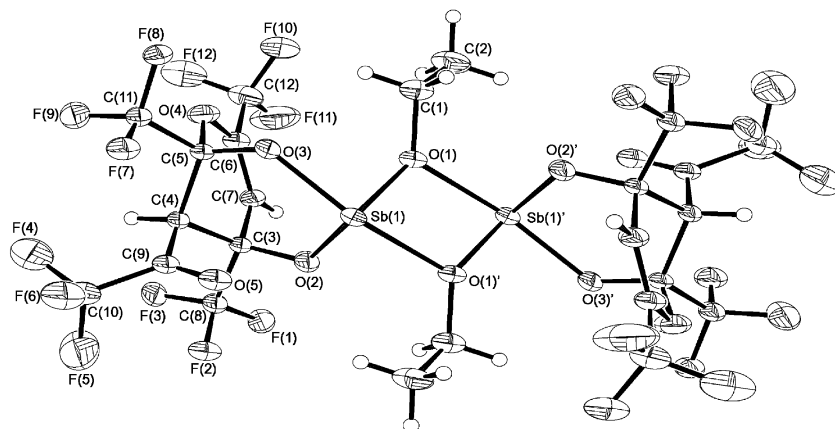
Fig. 4 The dimeric structure of **3** showing the asymmetric unit and the labelling scheme. Ellipsoids are at the 30% probability level. Selected metrical data: Sb(1)–O(1) 2.009(3), Sb(1)–O(1') 2.329(3), Sb(1)–O(2) 1.971(3), Sb(1)–O(3) 2.052(3), O(1)–C(1) 1.459(6), O(2)–C(3) 1.405(4), O(3)–C(5) 1.353(5), O(4)–C(5) 1.447(5), O(4)–C(6) 1.361(5), O(5)–C(9) 1.200(5), C(1)–C(2) 1.486(8), C(3)–C(4) 1.562(5), C(3)–C(7) 1.500(5), C(3)–C(8) 1.534(6), C(4)–C(5) 1.555(5), C(4)–C(9) 1.514(5), C(5)–C(11) 1.536(6), C(6)–C(7) 1.316(6), C(6)–C(12) 1.498(6), C(9)–C(10) 1.547(6) Å; O(1)–Sb(1)–O(1') 70.37(12), O(1)–Sb(1)–O(2) 76.83(11), O(1)–Sb(1)–O(3) 153.72(12), O(2)–Sb(1)–O(1') 93.95(13), O(2)–Sb(1)–O(3) 89.78(12), O(1')1–Sb(1)–O(3) 88.43(12), Sb(1)–O(1)–Sb(1') 109.63(12)° (symmetry operation: −x, −y, −z).
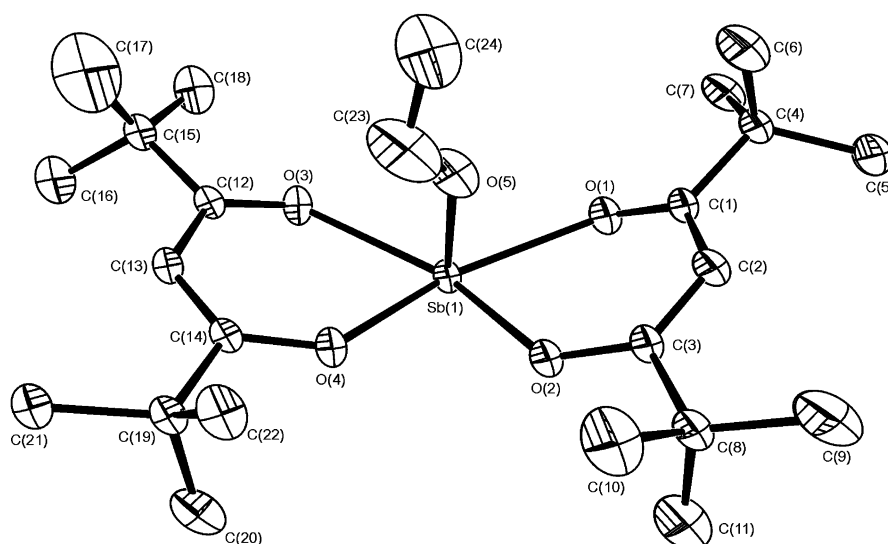

Fig. 5 The structure of **4** showing the asymmetric unit and the labelling scheme; ellipsoids are at the 30% probability level. Selected metrical data: Sb(1)–O(1) 2.346(2), Sb(1)–O(2) 2.089(2), Sb(1)–O(3) 2.395(2), Sb(1)–O(4) 2.089(2), Sb(1)–O(5) 1.923(2), O(1)–C(1) 1.257(4), O(2)–C(3) 1.301(3), O(3)–C(12) 1.248(3), O(4)–C(14) 1.299(3), O(5)–C(23) 1.330(5) Å; O(1)–Sb(1)–O(2) 79.13(8), O(1)–Sb(1)–O(3) 121.02(8), O(1)–Sb(1)–O(4) 155.48(8), O(1)–Sb(1)–O(5) 76.98(11), O(2)–Sb(1)–O(3) 156.11(8), O(2)–Sb(1)–O(4) 78.81(8), O(2)–Sb(1)–O(5) 91.61(11), O(3)–Sb(1)–O(4) 78.66(8), O(3)–Sb(1)–O(5) 81.78(11), O(4)–Sb(1)–O(5) 93.06(11)°.

Å]. The planes defined by O(1)–Sb(1)–O(1') and O(2)–Sb(1)–O(3) are at right angles (93.4°) leaving a vacancy in the antimony coordination sphere for a stereochemically active lone pair, though the geometry about the metal does not approximate to a regular polygon. Overall, the molecule is dimeric in which the two halves of the dimer are linked by a bridging ethoxy group. The longest of the Sb–O bonds can be attributed to the bridging Sb(1)–O(1') bond [2.329(3) Å] while the dihydropyran ring and the ethoxide form equally strong Sb–O interactions [Sb(1)–O(1): 2.009(3); Sb(1)–O(2): 1.971(3); Sb(1)–O(1): 2.052(3) Å].

Perhaps surprisingly in the light of the dimeric nature of **3**, heteroleptic Sb(OEt)(thd)₂ (**4**) remains monomeric (Fig. 5). The geometry at antimony is octahedral in which one site, *trans* to the Sb–OEt bond, is occupied by a stereochemically active lone pair. The shortest Sb–O bond involves the ethoxide [Sb(1)–O(5) 1.923(2) Å], while each thd unit bonds the metal in the same asymmetric manner as seen in **1** and **2** [Sb(1)–O(2) 2.089(2), Sb(1)–O(4) 2.089(2); Sb(1)–O(1) 2.346(2), Sb(1)–O(4) 2.395(2) Å]. Short and long Sb–O bonds are again mutually *trans*, replicating the features of **1** and **2**.

Conclusions

Antimony tris-β-diketonates Sb(thd)₃ and Sb(fod)₃ can be prepared in a straightforward manner from Sb(OEt)₃ and the β-diketonate. In contrast, attempts to prepare Sb(hfac)₃ have been unsuccessful and instead, a compound analysing as Sb(OEt)(hfac)₂, but in which the two β-diketonate ligands have coupled to yield a 3,4-dihydro-2*H*-pyran ring, is isolated. It appears that the two CF₃ groups are required to aid carbanion formation in this reaction, and that the metal also plays a key role as there is no precedent for this reaction among other M(hfac)₂ or M(hfac)₃ species which are widely known. Heteroleptic Sb(OR)₃ ₋ ₙ(β-dk)ₙ (*n* = 1, 2) can be prepared by the addition of one or two equivalents of β-diketonate ligand to Sb(OR)₃. The structure of Sb(OEt)(thd)₂ shows that compounds of this type are monomeric. Related Sb(v) compounds *e.g.* Sb(OEt)₄(thd) can be prepared similarly, and in these the antimony adopts an octahedral coordination. Despite promising volatility, preliminary APCVD with **1** or AACVD with either **2** or **3** failed to deposit an antimony-containing thin film.

References

1 P. W. Haycock, G. A. Horley, K. C. Molloy, C. P. Myers, S. A. Rushworth and L. M. Smith, *Chem. Vap. Deposition*, 2001, **7**, 191.
2 P. W. Haycock, G. A. Horley, K. C. Molloy, C. P. Myers, S. A. Rushworth and L. M. Smith, *J. Phys. IV (France)*, 2001, **11**, Pr3.
3 G. A. Horley, M. F. Mahon, K. C. Molloy, M. M. Venter, P. W. Haycock and C. P. Myers, *Inorg. Chem.*, 2002, **41**, 1652.
4 G. A. Horley, M. F. Mahon, K. C. Molloy, P. W. Haycock and C. P. Myers, *Inorg. Chem.*, 2002, **41**, 5052.
5 M. Tiitta and N. Lauri, *Chem. Vap. Deposition*, 1997, **3**, 167.
6 L. G. Hubert-Pfalzgraf, *Appl. Organomet. Chem.*, 1992, **6**, 627.
7 A. R. Siedle, *Diketones* in *Comprehensive Coordination Chemistry*, eds. R. D. Gillard, J. A. McCleverty and G. Wilkinson, Pergamon Press, Oxford, 1987, vol. 2, p. 365.
8 R. C. Mehrotra, *Pure Appl. Chem.*, 1988, **60**, 1349.
9 R. C. Mehrotra, R. Bohra and D. P. Gaur, *Metal Beta-diketonates and Allied Derivatives*, Academic Press, London, 1978.
10 A. P. Pisarevskii and L. I. Martynenko, *Koord. Khim.*, 1994, **20**, 324.
11 V. K. Jain, R. Bohra and R. C. Mehrotra, *Synth. React. Inorg. Met.-Org. Chem.*, 1979, **9**, 491.
12 R. C. Mehrotra and A. K. Rai, *Indian J. Chem.*, 1966, **4**, 537.
13 C. Gérard, E. A. C. Lucken and G. Bernardinelli, *J. Chem. Soc., Perkin Trans. 2*, 1986, 879.
14 L. Korte, D. Mootz, M. Scherf and M. Wiebcke, *Acta Crystallogr., Sect. C*, 1985, **44**, 1128.
15 J. Kroon, J. B. Hulscher and A. F. Peerdeman, *J. Organomet. Chem.*, 1972, **37**, 297.
16 V. K. Jain, R. Bohra and R. C. Mehrotra, *J. Organomet. Chem.*, 1980, **184**, 57.
17 T. B. Brill and N. C. Campbell, *Inorg. Chem.*, 1973, **12**, 1884.
18 G. M. Sheldrick, in SHELXS 86, A Computer Program for Crystal Structure Determination, University of Göttingen, Göttingen, 1986.
19 G. M. Sheldrick, in SHELXL 97, A Computer Program for Crystal Structure Refinement, University of Göttingen, Göttingen, 1997.
20 P. McArdle, *J. Appl. Crystallogr.*, 1995, **28**, 65.
21 J. D. Hepworth, *Pyrans and Fused Pyrans: Synthesis and Applications* in *Comprehensive Heterocyclic Chemistry*, eds. A. R. Katritzky and C. W. Rees, Pergamon Press, Oxford, 1984, vol. 3, p. 737.
22 G. Desimoni and G. Toccomi, *Chem. Rev.*, 1975, **75**, 651.
23 C. W. Smith, D. G. Norton and S. A. Ballard, *J. Am. Chem. Soc.*, 1951, **73**, 5273.
24 R. I. Longley Jnr, W. S. Emerson and A. J. Blardinelli, *Org. Synth., Coll. Vol.*, 1963, **4**, 311.
25 F. Ebina, T. Uehiro, T. Iwamoto, Y. Ouchi and J. Yoshino, *J. Chem. Soc., Chem. Commun.*, 1976, 245.
26 A. Kamiyama, T. Noguchi, T. Kajiwara and T. Ito, *Inorg. Chem.*, 2002, **41**, 507.
27 Y.-B. Dong, M. D. Smith, R. C. Layland and H.-C. Loye, *Inorg. Chem.*, 1999, **38**, 5027.
28 J. H. Horton, J. Rasmusson, J. G. Shapter and P. R. Norton, *Can. J. Chem.*, 1998, **76**, 1559.
29 P. T. Brain, M. Buhl, H. E. Robertson, A. D. Jackson, P. D. Lickiss, D. MacKerracher, D. W. H. Rankin, D. Shah and W. Thiel, *J. Chem. Soc., Dalton Trans.*, 1998, 545.
30 A. C. Jones, T. J. Leedham, P. J. Wright, M. J. Crosbie, P. A. Lane, D. J. Williams, K. A. Fleeting, D. J. Otway and P. O'Brien, *Chem. Vap. Deposition*, 1998, **4**, 46.
31 A. C. Jones, T. J. Leedham, P. J. Wright, M. J. Crosbie, D. J. Williams, K. A. Fleeting, H. O. Davies, D. J. Otway and P. O'Brien, *Chem. Vap. Deposition*, 1998, **4**, 197.
32 G. K.-J. Chao, R. L. Sime and R. J. Sime, *Acta Crystallogr., Sect. B*, 1973, **29**, 2845.
33 P. K. Hon and C. E. Pfluger, *J. Coord. Chem.*, 1973, **3**, 67.