

## A Volatile Mixed-metal Yttrium–Barium Compound: Synthesis and Molecular Structure of $\text{BaY}_2[\mu\text{-OCH}(\text{CF}_3)_2]_4(\text{thd})_4$ (thd = 2,2,6,6-tetramethylheptane-3,5-dionato)

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The volatile compound,  $\text{Y}_2\text{Ba}[\text{OCH}(\text{CF}_3)_2]_4(\text{thd})_4$ , is obtained by treating a mixed-metal yttrium–barium hexafluoroisopropoxide derivative and yttrium tetramethylheptanedionate  $\text{Y}(\text{thd})_3$ ; its structure is based on a central  $\text{Ba}[\text{OCH}(\text{CF}_3)_2]_4^{2-}$  moiety connected to two  $\text{Y}(\text{thd})_2$  fragments *via* the alkoxide ligands; barium–fluorine interactions lead to a twelve-coordinated metal while Y is six-coordinate.

Interest in metal organic chemical vapour deposition (MOCVD) for the preparation of thin films of high temperature superconductors essentially  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  has grown recently. While there are satisfactory metal oxide sources for copper and yttrium, barium derivatives are less favourable in terms of vapour pressure and thermal stability. The most commonly used barium oxide source, the 2,2,6,6-tetramethyl-

heptane-3,5-dionate 'Ba(thd)<sub>2</sub>', also displays poor reproducibility of data and thus of behaviour which are dependent on synthesis and purification methods (and thus formulation), and storage conditions.<sup>1</sup> Incorporation of barium into a heterometallic species may be a means of overcoming some of these problems and improving its transport in MOCVD conditions.<sup>2</sup> While barium–copper β-diketonatoalkoxide spe-

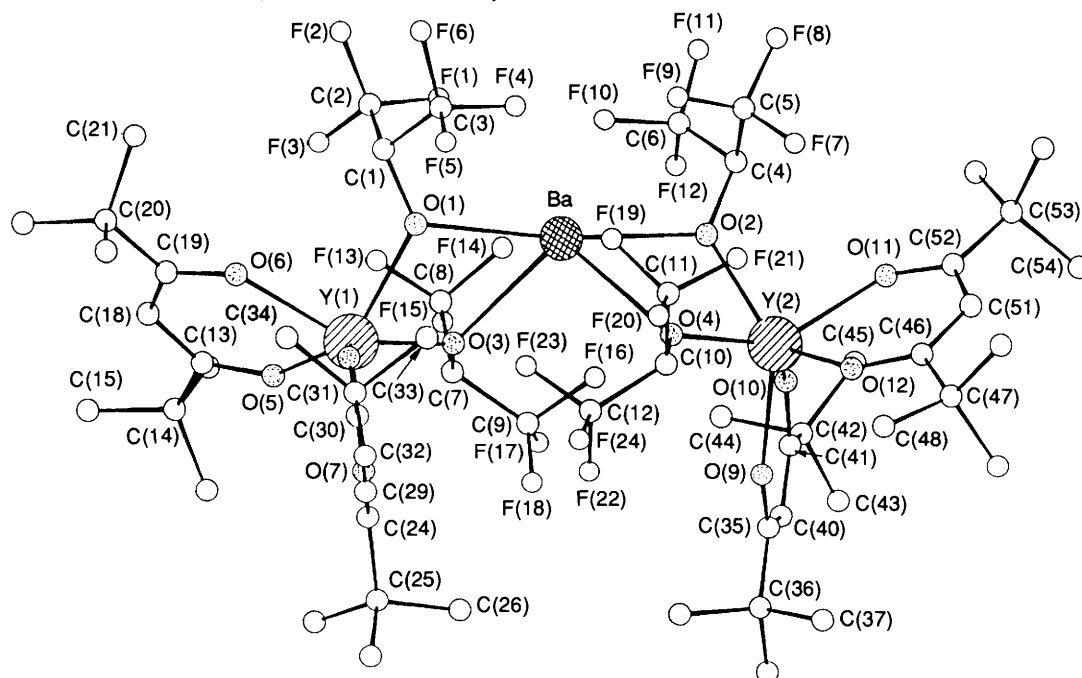
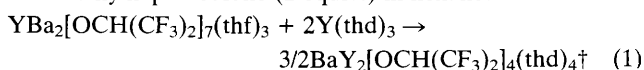


Fig. 1 Molecular structure of  $\text{BaY}_2[\mu\text{-OCH}(\text{CF}_3)_2]_4(\text{thd})_4$  showing the atom labelling scheme. Selected bond lengths (Å) and angles (°): Ba–O(R) 2.66 av., Y–O(R or thd) 2.22 av.; Y...Ba 4.00 av.; YOBa 108.8(4) av.,  $\angle \text{YBaY}$  129.35°.

cies of various stoichiometries and generally based on functional alcohols, alkoxyalcohols<sup>3,4</sup> or ethylene glycol,<sup>5</sup> have been reported; only one,  $\text{BaCu}_2[\text{OCMe}(\text{CF}_3)_2]_6$ , is volatile.<sup>6</sup> The only barium–yttrium species described and structurally characterized to date is the hexanuclear oxo species  $\text{Y}_4\text{Ba}_2(\mu_6\text{-O})(\mu\text{-OEt})_8(\text{thd})_6$ , however, its non-volatility precludes its possible use as single-source precursor.<sup>7</sup> Since the thermal decomposition of alkoxide derivatives might provide clean conversion to materials, we searched for an appropriate set of alkoxide and  $\beta$ -diketonate ligands that would provide stability and volatility of mixed-metal species and we now report the synthesis and characterization of the first volatile yttrium–barium derivative.

Metathesis reaction between the barium fluoroisopropoxide derivative<sup>8</sup> (obtained by the reaction between barium chips and 1,1,1,3,3,3-hexafluoropropan-2-ol in tetrahydrofuran (thf) and yttrium trichloride (stoichiometry 3.5 : 1) offered a heterometallic species  $\text{YBa}_2[\text{OCH}(\text{CF}_3)_2]_7(\text{thf})_9$  **1**. Although **1** is volatile, its sublimation (200–220 °C,  $10^{-3}$  mmHg) occurs with extensive decomposition. Further reaction between **1** and  $\text{Y}(\text{thd})_3$  in light petroleum (b.p. 40–60 °C) leads to progressive dissolution of **1** at room temp. with formation of a novel compound, poorly soluble in the reaction medium. Purification of the crude product by sublimation (150 °C,  $10^{-3}$  mmHg) offers a compound analysed as  $\text{BaY}_2[\text{OCH}(\text{CF}_3)_2]_4(\text{thd})$  **2** in high yield (74% [eqn. (1)]. Compound **2** appears as a thermodynamic 'sink', it could thus be obtained by various alternative routes,<sup>8</sup> although the yields were lower in general; yield 44% for treating **1** with tetramethylheptanedione (2 equiv.) in hexane.



<sup>†</sup>  $\text{Y}_2\text{Ba}[\text{OCH}(\text{CF}_3)_2]_4(\text{thd})_4$ : satisfactory elemental analysis (C,H,Y,Ba); Selected spectra data: IR  $\nu_{\text{cm}^{-1}}$  (mineral oil): 1602, 1583, 1572, 1556, 1545, 1508, ( $\nu_{\text{C=O}}$ ,  $\nu_{\text{C=C}}$ ); 610, 521, 493, 476, 414, 393, 378, ( $\nu_{\text{M-O}}$ ). NMR  $^1\text{H}$  ( $\text{CDCl}_3$ ): 5.68s [1H, CH(thd)]; 4.75 m, br [1H, OCH( $\text{CF}_3$ )<sub>2</sub>]; 1.09s (18H, Bu<sup>†</sup>); NMR  $^{19}\text{F}$  ( $\text{CDCl}_3$ ): -76.14,  $\Delta\nu_{1/2} = 26$  Hz ( $\text{CF}_3$ ).  $^{13}\text{C}$  NMR(MAS):  $\delta$  202.87, 202.28, 200.8, 200.58, 200.3, 200 (CO); 123.5m ( $\text{CF}_3$ );  $\delta$  93.07, 74.03 (CH, thd); 41.04, 40.77 (CBu<sup>†</sup>); 29.22, 28.94, 28.56, 28.30 ( $\text{CH}_3$ ); MS (EI, 70 eV, %):  $\text{F}_2\text{YBa}[\text{OCH}(\text{CF}_3)_2]_3(\text{thd})$  (2%),  $\text{YBa}[\text{OCH}(\text{CF}_3)_2]_2(\text{thd})_2$  (4%),  $\text{YBa}[\text{OCH}(\text{CF}_3)_2]_3(\text{thd})$  (1%),  $\text{YBa}[\text{OCH}(\text{CF}_3)_2]_2(\text{thd})$  (1%),  $\text{Y}(\text{thd})_3$  (47%),  $\text{Y}[\text{OCH}(\text{CF}_3)_2]_2(\text{thd})_2$  (6%),  $\text{FYBa}[\text{OCH}(\text{CF}_3)_2]_2(\text{thd})$  (2%),  $\text{Y}(\text{thd})_2(\text{BuCOCHCO})$  (100%),  $\text{Ba}(\text{BuCOCHCO})$  (7%),  $\text{CF}_3$  (4%),  $\text{Bu}$  (47%). TGA (5 °C min<sup>-1</sup>, 760 mmHg): percentage of mass loss in the range of 150–270 °C: 77%. First onset at 140 °C [ $\text{HOCH}(\text{CF}_3)_2$ ], second onset at 200 °C (fluoroisopropanol + thdH), last onset at 220 °C (thdH).

Crystal data for  $\text{C}_5\text{H}_8\text{F}_{24}\text{O}_{12}\text{BaY}_2$ : *M* 1716.4, triclinic, space group  $P\bar{1}$ , *a* = 10.922(5), *b* = 16.345(2), *c* = 21.926(4) Å,  $\alpha$  = 105.92(1),  $\beta$  = 97.59(3),  $\gamma$  = 100.74(2)°, *U* = 3628(2) Å<sup>3</sup>, *D*<sub>c</sub> = 1.57 g cm<sup>-3</sup>, *Z* = 2, (*MoK*α) = 22.4 cm<sup>-1</sup>.

Data were collected at -100 °C on an Enraf-Nonius CAD-4 diffractometer with graphite monochromated *MoK*α; a total of 6203 reflections were collected to a 2θ value of 36°, of which 5798 were unique; equivalent reflections were merged. Computations were performed by using CRYSTALS<sup>18</sup> adapted on a MicroVax II. The structure was solved by Patterson method and subsequent Fourier maps. Hydrogen atoms were placed in calculated positions (C-H 1.0 Å) with an isotropic thermal parameter 1.2 higher than that supporting carbon atoms. Non-hydrogen atoms were isotropically refined, except Y and Ba which were refined anisotropically. Least-square refinements based on 3490 observations [*I* > 3σ(*I*)] and 397 variable parameters with approximation in three blocks to the normal matrix were carried out to minimize the function  $w(|F_o| - |F_c|)^2$ , where *F*<sub>o</sub> and *F*<sub>c</sub> are the observed and calculated structure factors. The final cycle converged with *R* = 0.057 and *R*<sub>w</sub> = 0.064. Criteria for a satisfactory complete analysis were the ratios of rms shift to standard deviation being less than 0.1 and no significant feature in the final difference map. Empirical absorptions corrections using DIFABS<sup>19</sup> were made.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre, see Notice to Authors, Issue No. 1.

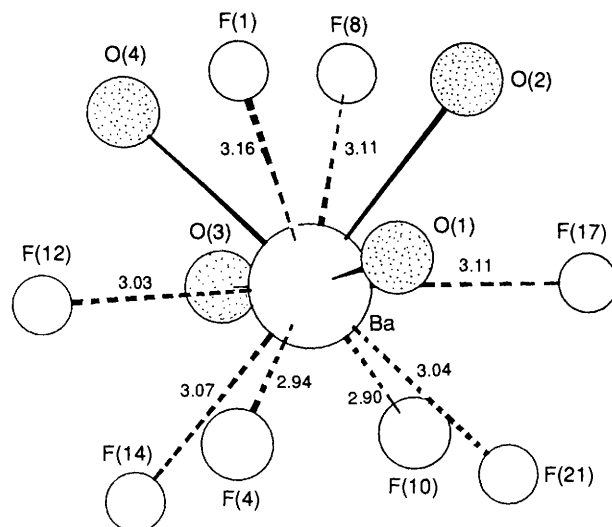


Fig. 2 Surrounding of the barium atom showing the Ba–O bonds as well as the secondary Ba···F interactions. The distances are given in Å.

Compound **2** has been characterized by FTIR, mass spectrometry,  $^1\text{H}$ ,  $^{19}\text{F}$  NMR and  $^{13}\text{C}$  MAS NMR spectroscopy and X-ray diffraction. Its thermal behaviour has been studied by thermogravimetric analysis and vapour pressure measurements. The IR spectrum of **2** displays the absorption bands of both fluoroisopropoxide and  $\beta$ -diketonate ligands, as well as  $\nu_{\text{Y-O}}$  and  $\nu_{\text{Ba-O}}$  vibrations at 521, 493, 476, 414, 393, 378 cm<sup>-1</sup>. The frequencies and the number of absorption bands in the C=O and C=C region support the formation of a novel compound as well as the diminution of the symmetry around the metal with respect to  $\text{Y}(\text{thd})_3$ .

Single crystals of **2** suitable for X-ray analysis were obtained by crystallization of the sublimate in light petroleum. The crystal structure determination established the connectivity between the different metals and thus the heterometallic nature of **2**; its molecular structure is shown in Fig. 1. Compound **2** corresponds to a trinuclear heterometallic species  $\text{BaY}_2[\mu\text{-OCH}(\text{CF}_3)_2]_4(\text{thd})_4$ , which presents an open, bent structure ( $\angle \text{YBaY}$  129.35°) with alternate Y and Ba atoms. The different metals are linked by fluoroisopropoxide bridges, while all the  $\beta$ -diketonate ligands are borne by the yttrium atoms; Ba–O bond lengths 2.63(1)–2.68(1) Å. These Ba–O bonds are short but are comparable with the values observed for  $\mu_2$ -alkoxide Ba–O distances such as in  $\text{BaCu}_2[\text{OCMe}(\text{CF}_3)_2]_6$  (av. 2.64 Å) or in  $\text{H}_3\text{Ba}_6\text{O}(\text{OBu}^{\dagger})_{11}(\text{OCe}(\text{CH}_2\text{O})(\text{thf})_3)$  (av. 2.63 Å).<sup>10</sup> The Y–O bond lengths are similar for alkoxide and tetramethylheptanedionate ligands (av. 2.23 Å). They fall in the range of the values observed for the Y–O(thd) distances in the structurally characterized tetramethylheptanedionates  $\text{Y}(\text{thd})_3$  and  $[\text{Y}(\text{thd})_3\text{H}_2\text{O}]_2$ <sup>11</sup> as well as for the  $\mu_2$ -alkoxide Y–O distances in  $\text{Y}_3(\text{OC}_2\text{H}_4\text{OMe})_5(\text{acac})_4$ ,  $\text{Y}_5\text{O}(\text{OPr}^i)_{13}$  or  $[\text{Y}(\text{OC}_2\text{H}_4\text{OMe})_3]_{10}$ <sup>12</sup> for instance. The yttrium atoms have a quite regular hexacoordinate surrounding, the angles O(1)–Y(1)–O(3) and O(2)–Y(2)–O(4) of the bridges (av. 74.8°) being comparable with the bite of the  $\beta$ -diketonate moiety (av. 74.7°) ensuring a trigonal prismatic geometry. The OBaO angles of the bridges are small (av. 62.3 and 61.4°), less strained YOBa angles [108.8(4)° av.] account for Y···Ba distances of 4.00 Å. The coordination polyhedron of the central barium atom formed by the four alkoxide type oxygen atoms is supplemented by interactions with eight fluorine atoms (Ba···F 2.9–3.16 Å) (the sum of the van der Waals radii is 3.57 Å) (Fig. 2), which act as secondary bonds<sup>13</sup> leading finally to a twelve-coordinate metal. A similar environment for barium has been observed in  $\text{BaCu}_2[\text{OCMe}(\text{CF}_3)_2]_6$ , and short M···F contacts appear to be a common feature for fluorinated alkoxides or  $\beta$ -diketonate derivatives, especially for large elements such as alkaline earth

metals or lanthanides.<sup>14</sup> The solid-state structure was also supported by <sup>13</sup>C MAS NMR, which was used as an additional tool in order to establish that the fluorinated ligands were authentic fluoroisopropoxides.<sup>15</sup> The surrounding of the different metals with encapsulation of the central barium atom results in a compound relatively stable in the atmosphere.

The <sup>1</sup>H and <sup>19</sup>F NMR spectra of compound **2** in C<sub>6</sub>D<sub>6</sub>/C<sub>6</sub>F<sub>6</sub> (1:2) or CDCl<sub>3</sub> solutions account for the retention of the solid-state structure. The <sup>19</sup>F NMR signal, quite broad with the F–H coupling being generally not resolved, is detected at high field with respect to the free alcohol.

Y<sub>2</sub>Ba[μ-OCH(CF<sub>3</sub>)<sub>2</sub>]<sub>4</sub>(thd)<sub>4</sub> appears as monomeric discrete molecules in the solid and is volatile. The mass spectrum exhibits several mixed-metal Y–Ba fragments at *m/z* 949, 927, 911 and 743. Compound **2** can be sublimed without disproportionation or decomposition at below 160 °C. Vapour pressure measurements confirm that the compound is well behaved in the temperature range 90–140 °C (vapour pressure 0.015 mmHg at 130 °C).<sup>16</sup> Thermogravimetric analysis under nitrogen indicates several mass losses corresponding successively to the elimination of the fluorinated ligands and to the β-diketone as shown by FTIR analysis of the volatiles. Preliminary thermal decomposition experiments (285–300 °C,) in a hot wall reactor on silica as a substrate led essentially to the deposition of oxides, Y<sub>2</sub>O<sub>3</sub> and Ba<sub>4</sub>Y<sub>2</sub>O<sub>7</sub>, with only trace amount of BaF<sub>2</sub> on the basis of scanning electron microscopy (SEM) and X-ray diffraction data.<sup>17</sup>

A similar approach to built up mixed-metal species, but using 1,1,1,3,3,3-hexafluoro-2-methylpropan-2-ol OHCMe(CF<sub>3</sub>)<sub>2</sub> as the alcohol, led to quite different results with formation of homoleptic hexafluoro-2-methyl-2-propoxide or tetramethylheptanedionatohexafluoro-2-methyl-2-propoxide mixed-metal species with a Ba–Y 1:1 stoichiometry but displaying less interesting solubility and/or volatility characteristics.

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- The isolated product was shown by X-ray diffraction to correspond to Ba<sub>5</sub>(OH)[OCH(CF<sub>3</sub>)<sub>2</sub>]<sub>5</sub>(thf)<sub>4</sub>(H<sub>2</sub>O). No difference in the nature of the products was observed by using the Ba derivative formed *in situ* or isolated. F. Labrize, L. G. Hubert-Pfalzgraf and J. P. Vincent, to be published.
- Compound **1** has been characterized by microanalysis (C, H, Y, Ba); IR/cm<sup>-1</sup>: 534, 521, 460, 399 ν<sub>M–O</sub>; <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>/C<sub>6</sub>F<sub>6</sub> 1:3): δ 5.37 (sept, *J* 6.5 Hz), 4.84 (sept, *J* 6.5 Hz), 4.72 m, 4.5 sept, *J* 6.5 Hz) (1:2:3:1, 7H, CH); 3.95 m (6H, thf), 2.15 m (6H, thf); <sup>19</sup>F NMR (C<sub>6</sub>D<sub>6</sub>/C<sub>6</sub>F<sub>6</sub> 1:3): δ 73.37 s (Δν<sub>1/2</sub> 17 Hz), –77.15 s (Δν<sub>1/2</sub> 17 Hz), –77.55 br (Δν<sub>1/2</sub> = 70 Hz), –79.4 s (Δν<sub>1/2</sub> = 17 Hz) (1:1:4:1, CF<sub>3</sub>) (sept = septuplet); an X-ray analysis established the connectivity between the metals but the structure could not be solved owing to disorder problems while a destructive phase transition (τ –10 °C) precluded data collection at low temperature. A. Albinati, unpublished results.
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