

# Synthesis, Characterization and Molecular Structures of Yttrium Trifluoroacetate Complexes with O- and N-Donors: Complexation vs. Hydrolysis

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Dehydration and complexation reactions of  $[\text{Y}(\text{TFA})_3(\text{H}_2\text{O})_3]$  (**1**; TFA =  $\text{O}_2\text{CCF}_3$ ) were investigated with O- and N-donor ligands in order to obtain suitable precursors for MOD (Metal Organic Deposition). Anhydrous adducts such as  $[\text{Y}_2(\mu, \eta^2\text{-TFA})_4(\eta^1\text{-TFA})_2(\text{OHC}_2\text{H}_4\text{O}i\text{Pr})_4]$  (**3**),  $[\text{Y}_2(\mu, \eta^2\text{-TFA})_4(\eta^1\text{-TFA})_2(\text{OHC}_2\text{H}_4\text{OC}_2\text{H}_4\text{OMe})_2]$  (**4**), or  $[\text{Y}(\text{TFA})_3(\text{triglyme})]$  (**5**) were isolated. The reactions with N-donor ligands are more complex and afford mixed-ligand derivatives such as  $[\text{Y}(\text{TFA})_3(\text{H}_2\text{O})_2(\text{LL})]_m$  [LL = TMEDA (**9**),  $\text{Me}_2\text{NC}_2\text{H}_4\text{NMeC}_2\text{H}_4\text{NMe}_2$  (**10**)] and, in the case of primary amines, yttrium oxohydroxo

derivatives such as  $[\text{H}_3\text{O}][\text{Y}_3(\mu_3\text{-OH})(\mu\text{-O})_3(\eta^1\text{-TFA})_3(\text{H}_2\text{O})_6(\text{en})_3]$  (**6**; en =  $\text{NH}_2\text{C}_2\text{H}_4\text{NH}_2$ ). All complexes were characterized by elemental analysis, FT-IR, and by single-crystal X-ray diffraction for **3**, **4**, and **6**. All structurally characterized complexes contain on eight-coordinate Y centers. Perfluorobutyrate and difluoroacetate derivatives were also prepared.

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## Introduction

Perfluorocarboxylate derivatives have been used as a source of fluorides by pyrolysis for glasses,<sup>[1]</sup> as a source of metal films for late transition metals, especially silver, by CVD techniques,<sup>[2]</sup> and have been considered for high Tc superconductors.<sup>[3]</sup> Trifluoroacetate (TFA) derivatives are currently used for elaboration of high Tc superconductor coatings by MOD (Metal Organic Deposition),<sup>[4a]</sup> a low-cost approach by comparison with vacuum approaches such as MOCVD (Metal Organic Chemical Vapour Deposition).<sup>[4b]</sup> This strategy proceeds via the formation of barium fluoride, thus avoiding the formation of more stable barium carbonate, during the thermal decomposition. However, the synthesis of the Ba, Y and Cu trifluoroacetates in situ starting from commercial acetates has led to lack of reproducibility in the quality of the coatings. This has been attributed to the volatility of the copper(II) derivative during the subsequent thermal treatment as well as to the presence of water. Lanthanide and yttrium trifluoroacetates associated with Al or Zn alkyls have also attracted interest as catalysts in various polymerization processes.<sup>[5]</sup> Although a large number of lanthanide trifluoroacetate complexes have been reported, often for their luminescence properties, few of

them are anhydrous. Most of them are mixed-ligand species such as  $[\text{Ln}(\text{TFA})_3\text{L}_2(\text{H}_2\text{O})]$  [L = pyzNO (pyrazine *N*-oxide)<sup>[6]</sup> or aza (2-azacyclononane)<sup>[7]</sup>] but species such as  $[\text{Ln}(\text{TFA})_3(\text{DMF})_2]$  (LL = bipy, *o*-phen)<sup>[8]</sup> are also known. Structural characterization remains scarce, although such adducts display a large structural diversity, as represented by the  $[\text{Ln}(\text{TFA})_3(\text{TMSO})_2]$  (TMSO = tetramethylene sulfide) derivatives,<sup>[9]</sup> which form infinite chains of dimers for Ln = La but discrete dimers for Ln = Nd, as well as  $[\text{Sm}_2(\mu, \eta^2\text{-TFA})_4(\eta^1\text{-TFA})_2(\text{aza})_2(\text{H}_2\text{O})_2] \cdot 2\text{aza}$ ,<sup>[7]</sup> ionic compounds for the  $\text{Ln}(\text{TFA})_3(\text{HMPA})_3$  adducts (Ln = La, Nd, Er) which are not isomorphous and are based on  $[\text{Er}(\eta^1\text{-TFA})_2(\text{HMPA})_4]^+$ ,  $[\text{Er}(\eta^1\text{-TFA})_2(\text{HMPA})_2(\text{H}_2\text{O})_3]^+$  or  $[\text{Nd}(\eta^2\text{-TFA})_2(\text{HMPA})_4]^+$  cations stabilized by a TFA counteranion.<sup>[10]</sup> Studies on yttrium derivatives remain quite scarce despite their interest in materials science.

We wish to report here the synthesis and characterization of yttrium fluorocarboxylate adducts with O- and N-donor ligands of various denticity. The anhydrous adducts  $[\text{Y}_2(\text{TFA})_6(\text{OHC}_2\text{H}_4\text{O}i\text{Pr})_4]$  (**3**) and  $[\text{Y}_2(\text{TFA})_6(\text{OHC}_2\text{H}_4\text{OC}_2\text{H}_4\text{OMe})_2]$  (**4**) and the ionic hydroxide derivative  $[\text{H}_3\text{O}][\text{Y}_3(\mu_3\text{-OH})(\mu\text{-O})_3(\eta^1\text{-TFA})_3(\text{H}_2\text{O})_6(\text{en})_3]$  (**6**; en =  $\text{NH}_2\text{C}_2\text{H}_4\text{NH}_2$ ) have been structurally characterized.

## Results and Discussion

The synthetic routes and reactivity of yttrium trifluoroacetate derivatives were investigated. The various compounds were isolated in high yields and characterized by

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elemental analysis and FT-IR and  $^1\text{H}$  NMR spectroscopy.  $[\text{Y}_2(\text{TFA})_6(\text{OHC}_2\text{H}_4\text{O}i\text{Pr})_4]$  (**3**),  $[\text{Y}_2(\text{TFA})_6(\text{OHC}_2\text{H}_4\text{OC}_2\text{H}_4\text{OMe})_2]$  (**4**), and  $[\text{H}_3\text{O}][\text{Y}_3(\mu_3\text{-OH})(\mu\text{-O})_3(\eta^1\text{-TFA})_3(\text{H}_2\text{O})_6(\text{en})_3]$  (**6**; en =  $\text{NH}_2\text{C}_2\text{H}_4\text{NH}_2$ ) were also characterized by single-crystal X-ray diffraction.

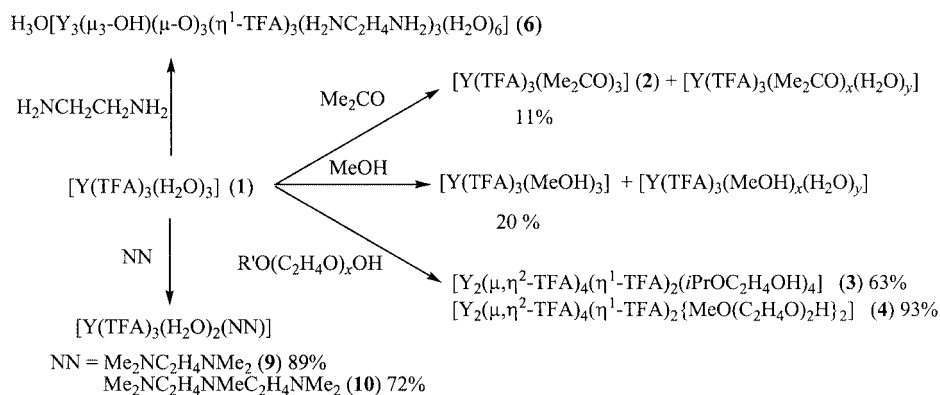
### Synthesis of Y Derivatives by Ligand Exchange and Thermal Dehydration

The classical, cost-efficient synthesis of yttrium trifluoroacetate by reacting the oxide with trifluoroacetic acid in refluxing toluene<sup>[11]</sup> proceeds with formation of water as by-product to afford the hydrate  $[\text{Y}(\text{TFA})_3(\text{H}_2\text{O})_3]$  (**1**). The presence of residual oxide was ascertained by absorption bands at 561 and 461  $\text{cm}^{-1}$  in the IR spectrum. Recrystallization of **1** from diethyl ether allowed elimination of  $\text{Y}_2\text{O}_3$ . Attempts to remove the water molecules (48 h, 140  $^\circ\text{C}$ ,  $10^{-4}$  Torr) were unsuccessful, probably due to the strong hydrogen bonding between the water molecules and the fluorinated ligand.<sup>[12]</sup> More efficient dehydration of **1** could be achieved at 200  $^\circ\text{C}$  in a furnace but some decomposition was observed and the anhydrous  $\text{Y}(\text{TFA})_3$  is very hygroscopic due to its high Lewis acidity. Methyl orthoformate has been used for the dehydration of  $\text{LnCl}_3 \cdot x\text{H}_2\text{O}$ ,<sup>[13]</sup> therefore its potential to dehydrate **1** was evaluated. If the preceding reaction was carried out in the presence of methyl orthoformate (stoichiometry 1:3), a different product was formed. The presence of methanol in the coordination sphere was confirmed by the reaction with  $[\text{Y}(\text{TFA})_3(\text{H}_2\text{O})_3]$  in refluxing methanol, which gives  $[\text{Y}(\text{TFA})_3(\text{MeOH})_x]$  (20%) and the partially dehydrated adduct  $[\text{Y}(\text{TFA})_3(\text{MeOH})_x(\text{H}_2\text{O})_y]$ . Attempts to use acetone as a ligand for access to anhydrous TFA derivatives, as reported for  $[\text{Cu}_2(\text{TFA})_4]_\infty$ ,<sup>[14]</sup> afforded the very hygroscopic species  $[\text{Y}(\text{TFA})_3(\text{Me}_2\text{CO})_3]$  (**2**) in low yield, the major species being a mixture of  $[\text{Y}(\text{TFA})_3(\text{H}_2\text{O})_x(\text{Me}_2\text{CO})_y]$  complexes which could not be crystallized out.  $[\text{Y}(\text{CHF}_2\text{CO}_2)_3(\text{H}_2\text{O})_3]$  was also prepared from the oxide and  $\text{CHF}_2\text{CO}_2\text{H}$  but, in contrast to **1**, it was insoluble in THF. Anhydrous perfluorobutyrate  $[\text{Y}(\text{O}_2\text{CC}_3\text{F}_7)_3]$  (**11**) was prepared from the oxide even in the absence of a dehydrating

reagent. However, high yields required long reactions times (3 d) and careful work-up due to its high volatility under vacuum. In contrast, the hydrate  $[\text{Y}(\text{O}_2\text{CC}_3\text{F}_7)_3(\text{H}_2\text{O})_2]$  (**12**) was obtained easily in nearly quantitative yield from  $[\text{Y}_2(\text{CO}_3)_3(\text{H}_2\text{O})_3]$  in refluxing toluene.

Ligand-exchange reactions with various polydentate N- or O-donors were more efficient and yielded dehydrated, partially dehydrated, or hydrolyzed adducts in either toluene or THF at room temp. Dissolution of **1** generally required an excess of ligand, especially in toluene. The O- and N-donor ligands behaved quite differently in their potential to give water-free adducts. Exchange reactions with  $i\text{PrOC}_2\text{H}_4\text{OH}$ ,  $\text{MeOC}_2\text{H}_4\text{OC}_2\text{H}_4\text{OH}$ , and triglyme ( $\text{MeOC}_2\text{H}_4\text{OC}_2\text{H}_4\text{OC}_2\text{H}_4\text{OMe}$ ) provided water-free  $[\text{Y}_2(\text{TFA})_6(i\text{PrOC}_2\text{H}_4\text{OH})_4]$  (**3**),  $[\text{Y}_2(\text{TFA})_6(\text{MeOC}_2\text{H}_4\text{OC}_2\text{H}_4\text{OH})_2]$  (**4**), and  $[\text{Y}(\text{TFA})_3(\text{MeOC}_2\text{H}_4\text{OC}_2\text{H}_4\text{OC}_2\text{H}_4\text{OMe})]$  (**5**), respectively (Scheme 1).

The reactions between  $[\text{Y}(\text{TFA})_3(\text{H}_2\text{O})_3]$  and N-donor Lewis bases (**B**) were more complex than those with O-donor ligands. Exchange reactions with TMEDA and  $\text{Me}_2\text{NC}_2\text{H}_4\text{NMeC}_2\text{H}_4\text{NMe}_2$  provided the partially dehydrated complexes  $[\text{Y}(\text{TFA})_3(\text{H}_2\text{O})_2(\text{Me}_2\text{NC}_2\text{H}_4\text{NMe}_2)]$  (**9**) and  $[\text{Y}(\text{TFA})_3(\text{H}_2\text{O})_2(\text{Me}_2\text{NC}_2\text{H}_4\text{NMeC}_2\text{H}_4\text{NMe}_2)]$  (**10**), respectively. However, in the presence of primary amines such as  $\text{H}_2\text{NC}_2\text{H}_4\text{NH}_2$  (en),  $\text{H}_2\text{NC}_2\text{H}_4\text{NMe}_2$ ,  $\text{H}_2\text{NC}_2\text{H}_4\text{NHC}_2\text{H}_4\text{NH}_2$ , and  $\text{H}_2\text{NC}_2\text{H}_4\text{NHC}_2\text{H}_4\text{OH}$ , part of the trifluoroacetate ligand was converted into a  $\text{BH}^+\text{TFA}^-$  salt to afford hydrolyzed metallic derivatives. In the case of ethylenediamine, the metallic species corresponds to an anionic trinuclear oxohydroxide  $[\text{Y}_3(\mu_3\text{-OH})(\mu\text{-O})_3(\eta^1\text{-TFA})_3(\text{H}_2\text{O})_6(\text{en})_3]^-$  stabilized by  $\text{H}_3\text{O}^+$  as counterion, all metals being eight-coordinate (see below). Adducts with similar formulae were obtained with other primary amines, namely the tridentate  $\text{NH}_2\text{C}_2\text{H}_4\text{NHC}_2\text{H}_4\text{X}$  (X =  $\text{NH}_2$ , OH) ligands, although these compounds were devoid of water. The various yttrium oxohydroxide trifluoroacetate complexes were often contaminated by some trifluoroacetate ammonium salts which were difficult to separate by crystallization or by sublimation. These results show that reactions between **1** and tertiary amines afford partially dehydrated adducts, while those with primary amines give



Scheme 1. Reactivity of **1** toward some O- and N-donors (all reactions at room temp.).

hydrolyzed products. The formation of **6** according to Equation (1) supposes the presence of more water than that resulting from **1**, the additional water molecules being provided either by the solvent or, more likely, by the hygroscopic character of **1**. An hydroxy Pr trifluoroacetate  $[\text{Pr}_2(\text{TFA})_3(\text{OH})(15\text{-crown-5})_2][\text{Pr}_2(\text{TFA})_8]$  has been reported by treatment of  $[\text{Pr}(\text{TFA})_3(\text{H}_2\text{O})_3]$  with 15-crown-5.<sup>[15]</sup>

### Physical Characteristics and Thermal Behavior

The various complexes display very intense broad absorption bands in their FT-IR spectra – generally two – at around  $1290\text{--}1100\text{ cm}^{-1}$  corresponding to the C–F vibrations.<sup>[16,17]</sup> Additional sharp bands due to the coordinated Lewis base are present as well but they are shifted downfield with respect to the free ligand, as illustrated for

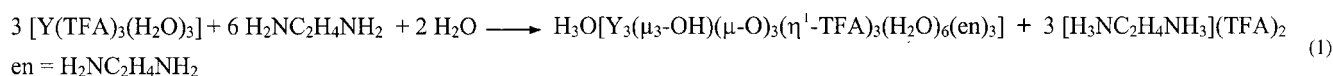


Table 1. IR data [ $\text{cm}^{-1}$ ] of the various yttrium fluorocarboxylate adducts.

Compound	$\nu(\text{CO}_2)$ $\nu_{\text{as}}(\text{CO}_2)$	$\nu_s(\text{CO}_2)$	$\nu(\text{M-O})$	$\nu(\text{OH})$ $[\nu(\text{NH})]$	Observation
$[\text{Y}(\text{TFA})_3(\text{H}_2\text{O})_3]$ ( <b>1</b> )	1760 sh, 1732 m, 1671 s, 1652 m, 1623 m, 1601 sh	1482 m, 1462 m	612 w, 523 w, 460 m	3695 m, 3667 w, 3626 w, 3611 w, 3433 br	air-stable.
$[\text{Y}(\text{TFA})_3(\text{Me}_2\text{CO})_3]$ ( <b>2</b> )	1682 vs	1456 s	633 w, 613 w, 604 w, 524 m, 500 w, 455 m	—	hygroscopic, gives $\text{Y}(\text{TFA})_3(\text{H}_2\text{O})_3$ in air.
$[\text{Y}_2(\text{TFA})_6(i\text{PrOC}_2\text{H}_4\text{OH})_4]$ ( <b>3</b> )	1738 s, 1674 s	1458 m	615 w, 605 w, 574 w, 522 w, 456 w	3160 br	air-stable for some hours, loses ligands in air; soluble in THF, toluene, EtOH.
$[\text{Y}_2(\text{TFA})_6(\text{MeOC}_2\text{H}_4\text{OC}_2\text{H}_4\text{OH})_2]$ ( <b>4</b> )	1747 s, 1674 s	1477 m	617 w, 606 w, 582 w, 537 w, 522 w, 460 w	3144 w, 3115 w	air-stable for some hours, soluble in THF, MeCN, EtOH, insoluble in toluene, hexane.
$[\text{Y}(\text{TFA})_3(\text{MeOC}_2\text{H}_4\text{OC}_2\text{H}_4\text{OC}_2\text{H}_4\text{OMe})]$ ( <b>5</b> )	1749 m, 1681 s	1462 s	653 w, 607 m, 523 m, 456 m	—	soluble in THF, MeOH, DME (comparable), insoluble in toluene, $\text{CHCl}_3$ .
$[\text{H}_3\text{O}][\text{Y}_3\text{O}(\text{OH})_3(\text{TFA})_3(\text{H}_2\text{NC}_2\text{H}_4\text{NH}_2)_3(\text{H}_2\text{O})_6]$ ( <b>6</b> )	1682 vs, 1599 s	1405 w	625 m, 599 m, 518 w, 468 m	3606 w, 3375 s, 3336 s, 3298 s, 3175 m	hygroscopic, soluble in THF, EtOH, MeOH, insoluble in $\text{CHCl}_3$ .
$[\text{H}_3\text{O}][\text{Y}_3\text{O}(\text{OH})_3(\text{TFA})_3(\text{H}_2\text{NC}_2\text{H}_4\text{NHC}_2\text{H}_4\text{NH}_2)_3]$ ( <b>7</b> )	1715 s, 1682 s, 1606 m, 1590 m	1456 m, 1436 w, 1418 w	603 m, 582 m, 501 m, 483 m, 459 w	3344 m, 3293 m, 3234 m, 3171 m	air-stable for some hours, soluble in EtOH, slightly soluble in THF.
$[\text{H}_3\text{O}][\text{Y}_3\text{O}(\text{OH})_3(\text{TFA})_3(\text{H}_2\text{NC}_2\text{H}_4\text{NHC}_2\text{H}_4\text{OH})_3]$ ( <b>8</b> )	1682 s, 1596 m	1375 w, 1446 m	600 w, 580 m, 552 m, 519 w, 466 m	3375 br, 3319 br, 3288 br. m	soluble in THF, insoluble in $\text{Et}_2\text{O}$ , toluene, hexane.
$[\text{Y}(\text{TFA})_3(\text{H}_2\text{O})_2(\text{Me}_2\text{NC}_2\text{H}_4\text{NMe}_2)]$ ( <b>9</b> )	1694 s	1460 s	604 w, 522 m, 453 m	3390 br, 3083 m	hygroscopic, soluble in THF, EtOH, acetone, insoluble in toluene.
$[\text{Y}(\text{TFA})_3(\text{H}_2\text{O})_2(\text{Me}_2\text{NC}_2\text{H}_4\text{NMe}_2\text{C}_2\text{H}_4\text{NMe}_2)]$ ( <b>10</b> )	1714 vs	1457 m, 1414 m	602 w, 551 w, 522 m, 453 m	3353 m	hygroscopic, soluble in THF, MeCN, EtOH, insoluble in toluene.
$[\text{Y}(\text{O}_2\text{CCF}_3)_3]$ ( <b>11</b> )	1694 s, 1643 w	1424 w	643 w, 585 w, 532 w, 464 w	—	air-stable, soluble in EtOH, $\text{H}_2\text{O}$ , slightly soluble in $\text{Et}_2\text{O}$ , insoluble in toluene.
$[\text{Y}(\text{H}_2\text{O})_2(\text{O}_2\text{CCF}_3)_3]$ ( <b>12</b> )	1745 m, 1660 vs	1455 m, 1378 m	639 w, 593 w, 555 w, 530 w, 475 w	3663 br, 3379 br	air-stable, soluble in EtOH, $\text{H}_2\text{O}$ , slightly soluble in $\text{Et}_2\text{O}$ ; insoluble in toluene.
$[\text{Y}(\text{O}_2\text{CCHF}_2)_3(\text{H}_2\text{O})_3]$	1734 m, 1695 m, 1625 s	1483 m, 1421 w	586 m, 484 m	3640 m, 3406 br	air stable, hygroscopic.

the alcohol adducts **3** and **4**. The absorption bands characteristic of the carboxylate ligands appear generally as several bands for the  $\nu_{\text{as}}(\text{CO}_2)$  stretch, with some around 1740–1715  $\text{cm}^{-1}$  and some at lower frequencies around 1680–1600  $\text{cm}^{-1}$ , suggesting trifluoroacetate ligands displaying different coordination modes such as bridging or bridging-chelating and monodentate (Table 1). Similar patterns have been observed for  $[\text{Sm}_2(\mu, \eta^2\text{-TFA})_4(\eta^1\text{-TFA})_2\text{-(aza)}_4(\text{H}_2\text{O})_2]\cdot 2\text{aza}^{[7]}$  and  $[\text{LaCu}(\text{bdmmpH})(\text{bdmmp})(\mu\text{-OH})(\text{TFA})_3]_2[\text{bdmmpH} = 2,6\text{-bis(dimethylaminomethyl)-4-methylphenol}]^{[18]}$ . The absorption band at 1682  $\text{cm}^{-1}$  for **6** and **8**, for instance, suggests the presence of monodentate TFA, in agreement with the frequency found for the dangling TFA of  $[\text{Y}(\eta^1\text{-TFA})_2(\text{H}_2\text{O})_6][\text{TFA}](18\text{-crown-6})^{[19]}$ . The presence of  $\eta^1\text{-TFA}$  ligands is also evidenced by the reduction of the intensity of the  $\nu_{\text{s}}(\text{CO}_2)$  absorption bands around 1403  $\text{cm}^{-1}$ . The presence of water molecules in the coordination sphere of the complexes with the N-donor ligands (**9** and **10**) is evidenced by bands between 3350 and 3700  $\text{cm}^{-1}$ .

The TGA patterns ( $\text{N}_2$ , 1 atm) of the perfluorobutyrate derivatives **11** and **12** account for their volatility. They decompose into yttrium fluoride and oxofluoride, respectively. Compound **12** decomposes between 320 and 370  $^\circ\text{C}$  after loss of water (up to 210  $^\circ\text{C}$ ), whereas **11** decomposes between 270 and 310  $^\circ\text{C}$ .

Anhydrous metal trifluoroacetate derivatives are less soluble in organic media than their hydrated counterparts, and the yttrium derivatives are also less soluble than the barium derivatives.<sup>[17]</sup> Complexation with organic ligands improves their solubility and the complexes have good solubility in polar solvents such as THF, DME, and alcohols. All the anhydrous yttrium trifluoroacetate complexes are slightly hygroscopic. As expected, the solubility in organic media also increases with the length of the fluoroalkyl chain, the solubility of  $[\text{Y}(\text{PFB})_3(\text{H}_2\text{O})_2]$  in MeOH, for example, is thus much better than that of  $[\text{Y}(\text{TFA})_3(\text{H}_2\text{O})_3]$ . Both compounds are actually more soluble in MeOH than in *i*PrO-C<sub>2</sub>H<sub>4</sub>OH. The low solubility of the various fluoroacetate compounds in nonpolar solvents precluded access to useful  $^1\text{H}$  or  $^{19}\text{F}$  NMR spectroscopic data (extensive dissociation was generally observed in CD<sub>3</sub>OD).

#### Molecular Structures of $[\text{Y}_2(\text{TFA})_6(\text{R}'\text{OH})_x]$ ( $\text{R}' = i\text{PrOC}_2\text{H}_4$ , $x = 4$ ; $\text{R}' = \text{MeOC}_2\text{H}_4\text{OC}_2\text{H}_4$ , $x = 2$ ) and of $[\text{H}_3\text{O}][\text{Y}_3(\mu\text{-O})_3(\mu_3\text{-OH})(\text{TFA})_3(\text{en})_3(\text{H}_2\text{O})_6]$

Compounds **3**, **4**, and **6** were characterized by low-temperature single-crystal X-ray diffraction. The structures of complexes **3** and **4** with the O-donor ligands are depicted in Figures 1 and 2, respectively. Two independent molecules (**3a** and **3b**) having similar metric parameters are present in the unit cell of **3**. Selected bond lengths and angles are collected in Table 2 and Table 3 for **3** and **4**, respectively. The Y–TFA adducts with O-donor Lewis bases are dinuclear. Their molecular structure is based on a  $\text{Y}_2(\mu, \eta^2\text{-TFA})_4(\eta^1\text{-$

$\text{TFA})_2$  core, the coordination sphere being completed by neutral ligands in order to achieve eight-coordination for the metals. As a result, the adduct **3** with isopropoxyethanol shows two different coordination modes, namely monodentate  $\eta^1\text{-}$  and bidentate  $\eta^2\text{-}$  for the alcohol, whereas 2-propoxyethoxyethanol ( $\text{HOC}_2\text{H}_4\text{OC}_2\text{H}_4\text{OMe}$ ) is tridentate in **4**. The Y–O bond lengths range from 2.280(3) to 2.437(3) Å in **4**. The Y– $\mu, \eta^2\text{-O}(\text{TFA})$  bonds [av. 2.329(5) and 2.334(3) Å for **3** and **4**, respectively] are longer than the corresponding Y– $\eta^1\text{-O}(\text{TFA})$  ones [2.301(5) and 2.300(3) Å]. As observed for an  $\eta^1\text{-TFA}$  barium derivative, the C–O bonds are slightly elongated by coordination [1.256(3) vs. 1.193(3) Å]. The coordination polyhedra of Y correspond to a square prism and a distorted square antiprism for **3** and **4**, respectively. The Y···Y distances have values of 4.484(2) (av.) and 4.464(5) Å for **3** and **4** respectively. They are thus longer than the Ln···Ln distances in  $[\text{Sm}_2(\mu, \eta^2\text{-TFA})_4(\eta^1\text{-TFA})_2(\text{aza})_4(\text{H}_2\text{O})_2]\cdot 2\text{aza}^{[7]}$  and  $[\text{Nd}_2(\mu, \eta^2\text{-TFA})_4(\eta^2\text{-TFA})_2(\text{TMSO})_2]^{[9]}$  despite the smaller size of the metal, and also much longer than for  $[\text{Y}_2(\text{TFA})_6(\text{bdmap})_2]^{2-}$  [bdmap = 1,3-bis(dimethylamino)-2-propoxide  $\{\text{OCH}(\text{CH}_2\text{NMe}_2)_2\}$ ].<sup>[20]</sup> The bridging coordination mode of the trifluoroacetate ligand is quite common for homometallic as well as heterometallic compounds such as  $[(\mu\text{-TFA})_2\text{Ln}(\mu\text{-CF}_3\text{CHO}_2)\text{AlR}_2(\text{THF})_2]_2$  (Ln = Nd, Y, Eu). The Y···F distances ( $>4.5$  Å) account for the absence of Y···F interactions in the solid state, in contrast to the lanthanide fluorinated alkoxides.<sup>[17b]</sup> Octacoordination appears as the preferred coordination number for all structurally characterized yttrium trifluoroacetate derivatives.

Compound **6** crystallizes in the rhombohedral space group  $R\bar{3}$  as a trinuclear anion and a  $\text{H}_3\text{O}^+$  hydroxonium cation with the overall formula  $[\text{H}_3\text{O}][\text{Y}_3(\mu_2\text{-O})_3(\mu_3\text{-OH})(\text{TFA})_3(\text{en})_3(\text{H}_2\text{O})_6]$ . The anion has  $C_3$  symmetry, with the O3 oxygen atom ( $\mu_3\text{-OH}$ ) and the  $\text{H}_3\text{O}^+$  ion both located on the  $C_3$  axis, with O3 capping the trinuclear  $[\text{Y}_3(\mu\text{-O})_3(\mu_3\text{-OH})]^{+2}$  unit (Figure 3). Selected bond lengths and angles are collected in Table 4. The Y–O bond lengths spread over the range 2.217(12) to 2.65(2) Å and follow the order  $\text{Y}-\mu\text{-O} < \text{Y}-\mu_3\text{-OH} < \text{Y}-\eta^1\text{-O}(\text{TFA}) < \text{Y}-\text{Ow}(\text{H}_2\text{O})$ . For the latter, two types of Y–Ow distances [2.49(2) and 2.64(2) Å] are observed. The Y– $\eta^1\text{-O}(\text{TFA})$  bond lengths of 2.44(2) Å (av.) are much longer than those in **3** and **4** despite the identical coordination numbers. The Y···O distances involving the dangling oxygen atoms have values of 3.636 Å. The Y–N bond distances [2.55(2) Å] are comparable to those observed, for instance, for  $[\text{Y}_2(\text{thd})_4(\mu, \eta^2\text{-bdmap})_2]$  (thd = 2,2,6,6-tetramethylheptane-3,5-dionate).<sup>[20]</sup> The Y···Y distance of 3.778(3) Å is in agreement with the data reported for the previous compound or for  $[\text{Cp}_6\text{Y}_3(\mu\text{-OMe})_3(\mu_3\text{-H}_2)\text{Li}_2(\text{THF})_6]^{[21]}$ . It is much shorter than for **3** or **4**, where the metals are bridged by the trifluoroacetate ligands, but longer than for most other polynuclear yttrium alkoxides. The TFA and ethylenediamine ligands are located below the  $\text{Y}_3$  plane on the same side as the hydroxide ligand, whereas the hydroxonium cation is located on the same side as the water molecules. As for the other derivatives, the structure of **6** displays no short Y···F ( $>5.127$  Å)



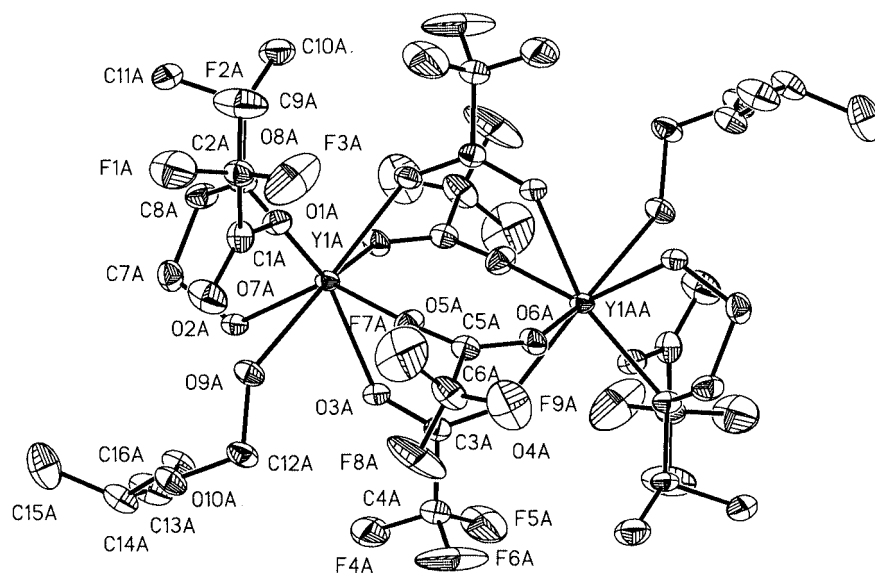


Figure 1. Molecular structure of **3** showing the atom numbering scheme (thermal ellipsoids at 30% probability).

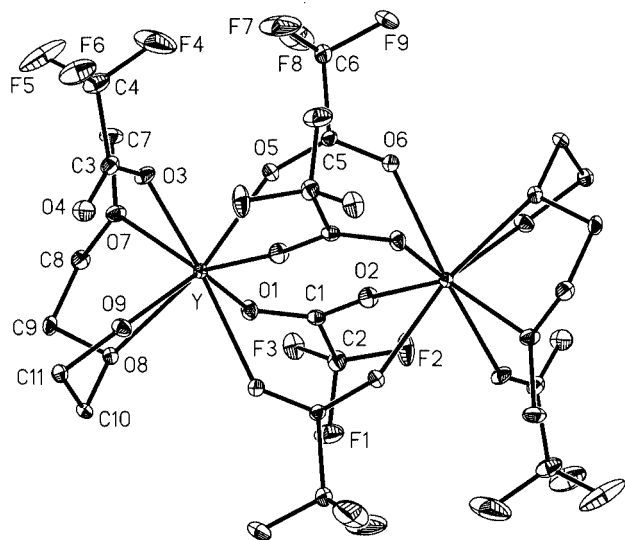


Figure 2. Molecular structure of **4** showing the atom numbering scheme (thermal ellipsoids at 30% probability).

Table 2. Selected bond lengths [Å] for **3a** and **3b** with estimated standard deviations in parentheses.<sup>[a]</sup>

Y1A–O5A	2.293(5)	Y2A–O1B	2.293(5)
Y1A–O1A	2.200(5)	Y2A–O5B	2.303(5)
Y1A–O4A#1	2.322(4)	Y2B–O4B#2	2.325(5)
Y1A–O3A	2.328(5)	Y2B–O3B	2.344(4)
Y1A–O6A#1	2.366(4)	Y2B–O6B#2	2.359(5)
Y1A–O9A	2.377(4)	Y2B–O7B	2.376(4)
Y1A–O7A	2.388(4)	Y2B–O9B	2.384(5)
Y1A–O8A	2.396(4)	Y2B–O8B	2.396(5)
Y1A...Y1A #1	4.484(2)	Y2B...Y2B#2	4.483(1)

[a] Symmetry transformations used to generate equivalent atoms: #1:  $-x, -y, -z$ ; #2:  $-x + 1, -y + 1, -z + 1$ .

or  $\mu_3\text{-OH}\cdots\text{F}$  ( $>4.44$  Å) interactions. In contrast, one observes two quite short  $\text{N}\cdots\text{F}$  interactions, namely  $\text{N1}\cdots\text{F1}$  and  $\text{N1}\cdots\text{F3}$ , with values of 3.744 and 3.821 Å respectively. These  $\text{N}\cdots\text{F}$  interactions are much shorter than those ob-

Table 3. Selected bond lengths [Å] for **4** with estimated standard deviations in parentheses.<sup>[a]</sup>

Y–O2#1	2.280(3)	Y–O5	2.297(3)
Y–O3	2.300(3)	Y–O6#1	2.363(3)
Y–O7	2.391(3)	Y–O1	2.397(3)
Y–O9	2.409(3)	Y–O8	2.437(3)
Y...Y #1	4.464 (5)		

[a] Symmetry transformations used to generate equivalent atoms: #1:  $-x, -y, -z$ .

served, for instance, for  $[\text{Ce}\{\text{OCH}(\text{CF}_3)_2\}_4(\text{tmeda})]$  (4.137–4.259 Å).<sup>[22]</sup> The  $\text{Y}\cdots\text{O}(\text{H}_2\text{O})$  distance of 4.793(3) Å excludes the presence of ion pairs. The  $\text{O}(\text{H}_2\text{O})\cdots\text{O}(\text{H}_2\text{O}, \text{O1w})$  distance of 3.26 Å shows that no strong hydrogen bonding exists. Metal complexes containing the hydroxonium cation remain scarce. Some examples are represented

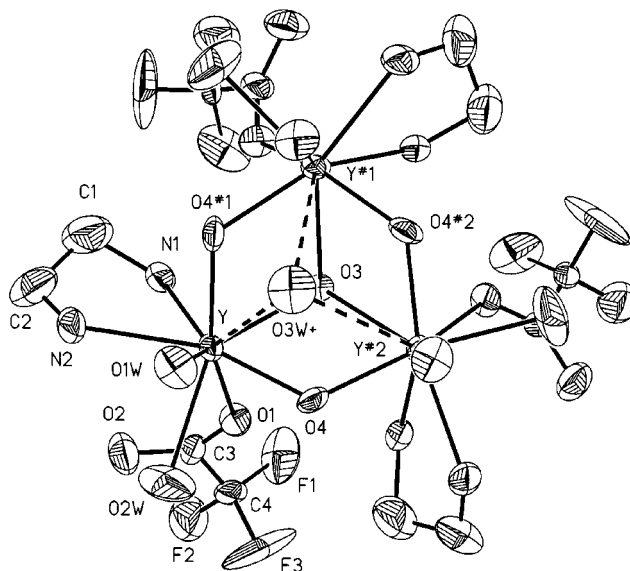


Figure 3. Molecular structure of **6** showing the atom numbering scheme (thermal ellipsoids at 30% probability).

by  $[\text{H}_3\text{O}][\text{Re}_3\text{Cl}_{10}(\text{H}_2\text{O})_2]\cdot 5\text{H}_2\text{O}$ <sup>[23]</sup> and by  $[\text{18-crown-6}](\text{H}_3\text{O})_2(\text{Hf}_2\text{F}_{10}\cdot 2\text{H}_2\text{O})\cdot 4\text{H}_2\text{O}$ <sup>[24]</sup> Trinuclear neutral metal oxocarboxylate cores  $[\text{M}_3(\mu_3\text{-O})(\text{TFA})_6(\text{H}_2\text{O})_3]$  ( $\text{M} = \text{Fe}, \text{Co}, \text{Mn}, \text{Ni}$ ) are quite common and have been used as building blocks for extended arrays.<sup>[25]</sup> On the other hand, reactions between fluoroacetates and amines are known to form ionic species, as observed, for instance, for bismuth with species such as  $[(\text{BH})_2\text{Bi}(\eta^1\text{-TFA})_5]$  ( $\text{B}$  being pyridine or diamines such as TMEDA or other tertiary diamines)

Table 4. Selected bond lengths [Å] and bond angles [°] for **6** with estimated standard deviations in parentheses.<sup>[a]</sup>

Bond lengths			
Y–O4#1	2.22(1)	Y–O4	2.29(1)
Y–O3	2.39(1)	Y–O1	2.43(2)
Y–N1	2.48(2)	Y–O1W	2.48(2)
Y–N2	2.55(2)	Y–O2W	2.65(2)
O3–Y#1	2.39(1)	O3–Y#2	2.39(1)
O4–Y#2	2.22(1)	Y...Y#1	3.778(3)
Y...Y#2	3.778(3)		
Bond angles			
O4#1–Y–O4	101.8(7)	O4#1–Y–O3	71.6(5)
O4–Y–O3	70.3(5)	O4#1–Y–O1	143.5(7)
O4–Y–O1	89.3(6)	O3–Y–O1	79.9(7)
O4#1–Y–N1	80.1(7)	O4–Y–N1	147.2(6)
O3–Y–N1	79.5(7)	O1–Y–N1	72.5(7)
O4#1–Y–O1W	77.2(7)	O4–Y–O1W	74.6(6)
O3–Y–O1W	126.1(9)	O1–Y–O1W	139.2(6)
N1–Y–O1W	136.4(6)	O4#1–Y–N2	81.0(5)
O4–Y–N2	144.7(8)	O3–Y–N2	140.6(5)
O1–Y–N2	109.5(6)	N1–Y–N2	68.1(8)
O1W–Y–N2	71.8(8)	O4#1–Y–O2W	141.2(8)
O4–Y–O2W	75.9(8)	O3–Y–O2W	137.9(5)
O1–Y–O2W	75.1(8)	N1–Y–O2W	122.8(10)
O1W–Y–O2W	64.7(9)	N2–Y–O2W	80.4(7)
Y–O3–Y#1	104.3(8)	Y–O3–Y#2	104.3(8)
Y#1–O3–Y#2	104.3(8)	Y#2–O4–Y	113.7(6)

[a] Symmetry transformations used to generate equivalent atoms: #1:  $-y, x - y - 1, z$ ; #2:  $-x + y + 1, -x, z$ .

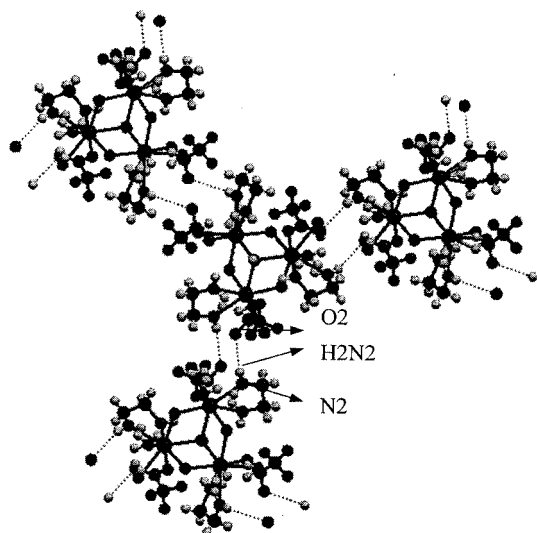


Figure 4. Inter-molecular H-bonding for **6** ( $\text{O2}\cdots\text{H2N2} = 2.70 \text{ Å}$ ,  $\text{O2}\cdots\text{N2} = 3.22 \text{ Å}$ ,  $\text{O2}\cdots\text{H2N2}\cdots\text{N2} = 119.9^\circ$ ).

where the cations interact with the dangling oxygen of the trifluoroacetate ligands by H-bonding (Figure 4).<sup>[26]</sup>

No reaction was observed between Y and Ba trifluoroacetate derivatives, for instance in methanol. This was also confirmed by the fact that the reaction between  $[\text{Ba}(\text{OH})_2(\text{H}_2\text{O})_8]$ , yttrium oxide, trifluoroacetic acid, and methyl orthoformate in refluxing toluene gave a mixture of the homometallic species  $[\text{Ba}(\text{TFA})_2]_m$ ,  $[\text{Y}(\text{TFA})_3(\text{H}_2\text{O})_3]$  and  $[\text{Y}(\text{TFA})_3(\text{MeOH})_x(\text{H}_2\text{O})_y]$  (IR evidence). In contrast, functional alcohols such as amino alcohols were able to promote the formation of heteronuclear assemblies.<sup>[27]</sup>

## Experimental Section

All manipulations were routinely performed under argon using Schlenk tubes and vacuum line techniques. Solvents were purified by standard methods. Trifluoroacetic (TFAH), perfluorobutyric (PFBH) and difluoroacetic acids (Aldrich) were stored over molecular sieves.  $[\text{Y}(\text{TFA})_3(\text{H}_2\text{O})_3]$  (**1**) was prepared by reacting the oxide with TFAH in refluxing toluene.<sup>[11]</sup> IR spectra were recorded as Nujol or as Fluorolub mulls on an IR-FTS 45 spectrometer. Elemental analyses were done at the Centre de Microanalyses du CNRS. IR data and general properties are collected in Table 1.

**[Y(TFA)<sub>3</sub>(Me<sub>2</sub>CO)<sub>3</sub>] (2):** Complex **1** (0.815 g, 1.69 mmol) was added to acetone (20 mL). Concentration after 2 d gave colorless crystals of **2**.  $\text{C}_{15}\text{H}_{18}\text{F}_9\text{O}_9\text{Y}$  (602.19): calcd. C 29.92, H 3.01, found C 30.03, H 3.10.

**[Y<sub>2</sub>(TFA)<sub>6</sub>(iPrOC<sub>2</sub>H<sub>4</sub>OH)<sub>4</sub>] (3):** *i*PrOC<sub>2</sub>H<sub>4</sub>OH (1.38 mL, 12.0 mmol) was added to a suspension of **1** (0.72 g, 1.5 mmol) in toluene (20 mL). After stirring for 14 h, concentration gave colorless crystals of **3** (0.60 g, 63%).  $\text{C}_{32}\text{H}_{48}\text{F}_{18}\text{O}_{20}\text{Y}_2$  (1272.5): calcd. C 30.20, H 3.80; found C 30.15, H 3.92.

**[Y<sub>2</sub>(TFA)<sub>6</sub>(MeOC<sub>2</sub>H<sub>4</sub>OC<sub>2</sub>H<sub>4</sub>OH)<sub>2</sub>] (4):** MeOC<sub>2</sub>H<sub>4</sub>OC<sub>2</sub>H<sub>4</sub>OH (0.43 mL, 3.6 mmol) was added to a suspension of **1** (0.58 g, 1.2 mmol) in toluene (20 mL). After stirring for 14 h, filtration gave a solid, which was redissolved in THF to yield colorless crystals of **4** (0.61 g, 93%).  $\text{C}_{22}\text{H}_{24}\text{F}_{18}\text{O}_{18}\text{Y}_2$  (1096.2): calcd. C 24.11, H 2.21; found C 24.33, H 2.34.

**[Y(TFA)<sub>3</sub>(MeOC<sub>2</sub>H<sub>4</sub>OC<sub>2</sub>H<sub>4</sub>OC<sub>2</sub>H<sub>4</sub>OMe)] (5):** Triglyme (0.5 mL, 2.74 mmol) was added to a solution of **1** (0.658 g, 1.37 mmol) in THF (15 mL). After stirring at room temp. for 14 h, concentration gave colorless crystals of **5** (0.52 g, 63%).  $\text{C}_{14}\text{H}_{18}\text{F}_9\text{O}_{10}\text{Y}$  (606.18): calcd. C 27.74, H 2.99; found C 27.94, H 3.10%.

**[H<sub>3</sub>O][Y<sub>3</sub>(μ<sub>3</sub>-OH)(μ-O)<sub>3</sub>(TFA)<sub>3</sub>(H<sub>2</sub>NC<sub>2</sub>H<sub>4</sub>NH<sub>2</sub>)<sub>3</sub>(H<sub>2</sub>O)<sub>6</sub>] (6):** A procedure similar to that of **5** but with ethylenediamine (0.66 mL, 9.92 mmol) and **1** (0.60 g, 1.24 mmol) in THF (15 mL) gave **6** (0.43 g).  $\text{C}_{12}\text{H}_{40}\text{F}_9\text{N}_6\text{O}_{17}\text{Y}_3$  (978.18): calcd. C 14.73, H 4.12, N 8.5; found C 16.20, H 4.30, N 9.15. <sup>1</sup>H NMR ( $\text{CD}_3\text{OD}$ ):  $\delta = 2.67$  (s, 12 H, CH<sub>2</sub>), 3.2 (s, Me) ppm. The product was sometimes contaminated with  $[\text{H}_3\text{NC}_2\text{H}_4\text{NH}_3][\text{TFA}]_2$ , thus precluding good analytical data.

**[H<sub>3</sub>O][Y<sub>3</sub>O(OH)<sub>3</sub>(TFA)<sub>3</sub>(H<sub>2</sub>NC<sub>2</sub>H<sub>4</sub>NHC<sub>2</sub>H<sub>4</sub>X)<sub>3</sub>] [X = NH<sub>2</sub> (7) and X = OH (8)]:** These complexes were prepared by a procedure similar to **6**.

**7:**  $\text{C}_{18}\text{H}_{45}\text{F}_9\text{N}_9\text{O}_{11}\text{Y}_3$  (1001.3): calcd. C 21.95, H 4.53, N 12.59; found C 23.48, H 4.12, N 13.20.

**8:**  $\text{C}_{18}\text{H}_{42}\text{F}_9\text{N}_6\text{O}_{14}\text{Y}_3$  (1004.3): calcd. C 21.53, H 4.22, N 8.37; found C 21.72, H 4.35, N 8.55.

Table 5. Crystal data and structure refinement for **3**, **4** and **6**.

	<b>3</b>	<b>4</b>	<b>6</b>
Empirical formula	C <sub>32</sub> H <sub>48</sub> F <sub>18</sub> O <sub>20</sub> Y <sub>2</sub>	C <sub>22</sub> H <sub>24</sub> F <sub>18</sub> O <sub>18</sub> Y <sub>2</sub>	C <sub>12</sub> H <sub>40</sub> F <sub>9</sub> N <sub>6</sub> O <sub>17</sub> Y <sub>3</sub>
Formula mass	1272.52	1096.23	978.23
Space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>R</i> $\bar{3}$
Crystal system	triclinic	triclinic	hexagonal
<i>a</i> [Å]	13.5965(2)	8.7109(1)	20.1921(17)
<i>b</i> [Å]	13.8952(3)	10.2862(2)	20.1921(17)
<i>c</i> [Å]	16.9439(4)	11.5968(2)	22.464(3)
$\alpha$ [°]	66.391(1)	96.221(1)	90
$\beta$ [°]	68.321(1)	103.231(1)	90
$\gamma$ [°]	66.182(1)	114.416(1)	120
<i>V</i> [Å <sup>3</sup> ]	2599.74(9)	896.58(3)	7932.1(14)
<i>Z</i>	2	1	6
Temperature [K]	160(2)	160(2)	163(2)
$\mu$ (Mo- <i>K</i> $\alpha$ ) [mm <sup>-1</sup> ]	2.352	3.388	3.343
$\theta$ range [°]	3.07 to 27.47	2.23 to 27.49	1.33 to 27.51
<i>hkl</i> ranges	–16 to 17, –18 to 17, –21 to 18	–11 to 10, –12 to 13, –15 to 13	123 to 20, –20 to 15, –23 to 5
No. of reflections collected	16204	6383	4747
No. of unique reflections ( <i>R</i> <sub>int</sub> )	11081 (0.0431)	4078 (0.0217)	4080 (0.0562)
Data/restraints/parameters	11081/0/649	4078/0/271	4080/10/ 159
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.062	1.245	1.073
<i>R</i> <sub>1</sub> , <i>wR</i> <sub>2</sub> [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )] <sup>[a]</sup>	0.0864, 0.2158	0.0409, 0.1165	0.0543, 0.1252
<i>R</i> <sub>1</sub> , <i>wR</i> <sub>2</sub> (all data)	0.1153, 0.2403	0.0547, 0.1582	0.0809, 0.1456
Residual electron density	2.038 and –1.033	1.153 and –1.224	0.155 and –0.172

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

[Y(TFA)<sub>3</sub>(H<sub>2</sub>O)<sub>2</sub>(Me<sub>2</sub>NC<sub>2</sub>H<sub>4</sub>NMe<sub>2</sub>)] (**9**) and [Y(TFA)<sub>3</sub>(H<sub>2</sub>O)<sub>2</sub>(Me<sub>2</sub>NC<sub>2</sub>H<sub>4</sub>NMeC<sub>2</sub>H<sub>4</sub>NMe<sub>2</sub>)] (**10**): Prepared by a procedure similar to **4**. Yields: 89% for **9** and 72% for **10**.

**9**: C<sub>12</sub>H<sub>20</sub>F<sub>9</sub>N<sub>2</sub>O<sub>8</sub>Y (580.19): calcd. C 24.84, H 3.47, N 4.93; found C 24.38, H 3.46, N 4.86.

**10**: C<sub>15</sub>H<sub>27</sub>F<sub>9</sub>N<sub>3</sub>O<sub>8</sub>Y (637.29): calcd. C 28.27, H 4.27, N 6.59; found C 28.15, H 4.13, N 6.70.

Treatment of **1** (0.67 g, 1.39 mmol) with Me<sub>2</sub>NC<sub>2</sub>H<sub>4</sub>NH<sub>2</sub> (0.46 mL, 4.16 mmol) in toluene or THF (20 mL) gave needles of Me<sub>2</sub>NC<sub>2</sub>H<sub>4</sub>NH<sub>3</sub>·TFA as the only crystalline species. IR:  $\tilde{\nu}$  = 1683 cm<sup>-1</sup> s, 1586 m, 1518 m, 1463 s, 1424 m; 598 w, 542 w, 520 w. X-ray data: *a* = 6.427(1), *b* = 18.124(4), *c* = 8.753(2) Å,  $\beta$  = 101.58(3)°, *V* = 998.8 Å<sup>3</sup>, space group *P*2<sub>1</sub>/*c*.

[Y(O<sub>2</sub>CCF<sub>3</sub>)<sub>3</sub>] (**11**): Perfluorobutyric acid (1.5 mL, 10.5 mmol) was added to a suspension of Y<sub>2</sub>O<sub>3</sub> (0.39 g, 1.74 mmol) in toluene (15 mL). After refluxing for 3 d, filtration and recrystallization from Et<sub>2</sub>O gave **11** by condensation into a cold trap during evaporation under vacuum (0.94 g, 75%). C<sub>12</sub>F<sub>21</sub>O<sub>6</sub>Y (728.00): calcd. C 19.8; found C 19.7.

[Y(H<sub>2</sub>O)<sub>2</sub>(O<sub>2</sub>CCF<sub>3</sub>)<sub>3</sub>] (**12**): Perfluorobutyric acid (3.3 mL, 25.3 mmol) was added to a suspension of Y<sub>2</sub>(CO<sub>3</sub>)<sub>3</sub>·3H<sub>2</sub>O (1.74 g, 4.2 mmol) in toluene (30 mL). After refluxing for 24 h, the precipitate was filtered, washed with hexane, and recrystallized from Et<sub>2</sub>O to give **12** (6.10 g, 95%). C<sub>12</sub>H<sub>4</sub>F<sub>21</sub>O<sub>8</sub>Y (764.03): calcd. C 18.86, H 0.53, found C 19.05, H 0.62.

[Y(O<sub>2</sub>CCH<sub>2</sub>F)<sub>3</sub>(H<sub>2</sub>O)<sub>3</sub>] (**13**): The same procedure as for **1** applied to Y<sub>2</sub>O<sub>3</sub> (452 mg, 2.0 mmol) and CHF<sub>2</sub>CO<sub>2</sub>H (0.4 mL, 6.0 mmol) in refluxing toluene for 32 h. Recrystallization from THF (75%). C<sub>6</sub>H<sub>9</sub>F<sub>6</sub>O<sub>9</sub>Y (428.03): calcd. C 16.84, H 2.12, found C 16.92, H 2.22.

All compounds were soluble in polar media (alcohols, THF, DME) but insoluble in CHCl<sub>3</sub> or hydrocarbons (aliphatic and aromatic).

**X-ray Crystallography of 3, 4, and 6**: Suitable crystals of **3**, **4**, and **6** were grown directly from the reaction media. X-ray single-crystal diffraction data were collected with a Nonius Kappa CCD dif-

fractometer. The data were processed with the DENZO reduction software package.<sup>[28]</sup> An absorption correction (XABS2)<sup>[29]</sup> was applied to the data of compound **3**. The structures were solved and refined on *F*<sup>2</sup> using SHELXTL.<sup>[30]</sup> All non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were included in the final refinement model in calculated positions with isotropic thermal parameters. The distribution of the C–F bond lengths is quite large due to disorder phenomena, which are also illustrated by high thermal factors. Crystal structure and refinement data are summarized in Table 5.

CCDC-227441 (for **3**), -227442 (for **4**), and -244549 (for **6**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

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