DOI: 10.1002/ejic.200600825

The Interplay between Yttrium and Barium or Copper Trifluoroacetates and *N*-Methyldiethanolamine: Synthesis of a Heterometallic Y_3Cu Trifluoroacetate Complex and a Homometallic Ba-TFA 1D Polymer

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Keywords: Heterometallic complexes / Yttrium / Copper / Barium / N,O ligands

The reactions between $[Y(TFA)_3(H_2O)_3]$ and either $[Cu(TFA)_2(MeOH)]$ or $[Ba(TFA)_2]_\infty$ in the presence of excess *N*-methyldiethanolamine ($mdeaH_2$) have been investigated in relation with their use as precursors for high Tc superconductors. They afford the heterometallic Y_3Cu complex $[CuY_3(\mu_3\text{-OH})(\mu\text{-}\eta^3:\eta^1\text{-mdeaH})_3(\mu_3\text{-}\eta^3:\eta^1:\eta^1\text{-mdeaH})_2(\eta^2\text{-TFA})(\mu,\eta^2\text{-TFA})_2](TFA)_2(H_2O)$ (**1**) and the homometallic Ba-TFA 1D polymer $[Ba_3(\eta^3\text{-mdeaH}_2)_2(\mu\text{-}\eta^3:\eta^1\text{-mdeaH}_2)_2(\eta^1\text{-TFA})_2(\eta^2\text{-TFA})_2(\mu_3\text{-}\eta^2:\eta^2:\eta^1\text{-TFA})_2]_{1\infty}$ (**2**), respectively, in high yield. These compounds were characterised by X-ray diffraction and FT-IR, ESR (for **1**) and NMR (for **2**) spectroscopy. Single-crystal X-ray diffraction studies show the versatile bonding modes of the trifluoroacetate and *N*-methyldiethanolamine ligands, with the former acting not only as a terminal (η^1 and η^2) or bridging-chelating (μ,η^2 and $\mu_3\text{-}\eta^2:\eta^2:\eta^1$) ligand but also as a counterion, whereas the latter, either protonated or partially deprotonated, binds the metal centres in a chelating (η^3) or bridging-chelating ($\mu,\eta^3:\eta^1$ and $\mu_3\text{-}\eta^3:\eta^1:\eta^1$) manner. The triangular Y_3 unit [3.480(6)–3.550(6) Å] in the cation of **1** consists of one nine-coordinate and two eight-coordinate Y atoms, the former of which are quite scarce in alkoxide chemistry. The unique feature of the 1D polymeric structure of **2** is the secondary F···cation bond, which has not been observed so far for TFA ligands. In addition, it is the only example where the Ba atom is linked to monodentate, bidentate and bridging trifluoroacetate ligands simultaneously.

Introduction

Fluorinated carboxylates, especially fluoroacetates, are the most common precursors for the elaboration of high Tc superconductor coatings.[1] For barium, their preferential decomposition into BaF_2 represents a means to avoid the formation of highly stable barium carbonate, which is detrimental to the superconducting properties. Mixed-metal species are a means to provide homogeneity at a molecular level in order to modify the reactivity pattern and solubility.[2] Various amino alcohols, such as 2,6-bis[(dimethylamino)methyl]-4-methylphenol (bdmmpH) and 1,3-bis(dimethylamino)propan-2-ol (bdmapH), have been shown to stabilize lanthanide–copper and alkaline-earth metal–copper heterometallic complexes with trifluoroacetate (TFA) ancillary ligands.[3] Compounds of different nuclearity, such as $[LaCu(TFA)_3(bdmmp)(bdmmpH)(OH)]_2$,[4] $LaCu_2(TFA)_4(bdmap)_3$,[5] $[LnCu(bdmapH)_2(hfacac)_2(TFA)L]$ [Ln = Y, Pr; hfacac = hexafluoroacetylactonate; L = 2-methyl-2,4,6-tris(trifluoromethyl)-1,3-dioxane-4,6-diolato],[6] $[LnCu_2(hfacac)(hfacacH)(bdmap)_3(OAc)(TFA)]$ (Ln = Pr, Nd),[6,7] $[Cu_3(bdmap)_3(TFA)_2]_2[Y_2(bdmap)_2(TFA)_6]$,[8] $[MCu(TFA)_2(bdmap)_2(H_2O)]_x$ (M = Ca, $x = 1$; M = Sr, $x = 2$),[9] $[Sr_2Cu_4(TFA)_4(bdmap)_6(OH)_2]$,[9] $[SrCu_2(TFA)_3(bdmap)_3]$[10] and $[BaCu_4(bdmap)_4(2\text{-PyO})_4(TFA)_2]$,[11] have been isolated. To the best of our knowledge, no amino alcohol has been shown to bridge yttrium and barium (or a lanthanide and an alkaline-earth metal) so far. Further studies are desirable to have a better understanding of the reactivity of these TFA species and to access heterometallic complexes with the right stoichiometry for the formation of $YBa_2Cu_3O_{7-x}$ films.

We have been interested in the design and synthesis of new homo- and heterometallic TFA derivatives related to high Tc superconductors.[12–14] The 1D coordination polymer $[Ba_3Cu_2(\mu,\eta^2\text{-TFA})_6(\mu,\eta^2\text{-dmea})_4(MeOH)_2\cdot 2MeOH]_{1\infty}$ was recently reported by our lab from the reaction between copper powder and $[Ba(TFA)_2]_\infty$ in methanol under air and in the presence of *N*-dimethylethanolamine (dmeaH).[12] The use of *N*-methyldiethanolamine ($mdeaH_2$) instead of dmeaH led to co-crystallisation of $[Ba(\eta^1\text{-TFA})_2(mdeaH_2)_2]$ and $[Cu(mdeaH)_2]$.[12] In continuation, we now wish to report the reactions between Y and Cu or Ba trifluoroacetates in the presence of *N*-methyldiethanolamine. These reactions afford the heterometallic, tetranuclear complex $[CuY_3(\mu_3\text{-OH})(\mu\text{-}\eta^3:\eta^1\text{-mdeaH})_3(\mu_3\text{-}\eta^3:\eta^1:\eta^1\text{-mdeaH})_2$

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$(\eta^2\text{-TFA})(\mu,\eta^2\text{-TFA})_2](TFA)_2(H_2O)$ (**1**) and the homometallic Ba TFA 1D polymer $[Ba_3(\eta^3\text{-mdeaH}_2)_2(\mu\text{-}\eta^2{:}\eta^1{:}\eta^1\text{-mdeaH}_2)_2(\eta^1\text{-TFA})_2(\eta^2\text{-TFA})_2(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^1\text{-TFA})_2]_{1\infty}$ (**2**), respectively, which were characterised by X-ray diffraction and FT-IR, X-band ESR (for **1**) and NMR (for **2**) spectroscopy.

Results and Discussion

Reactions between TFA Derivatives

The reaction between $[Y(TFA)_3(H_2O)_3]$ and $[Cu(TFA)_2(MeOH)]$ in the presence of $mdeaH_2$ afforded the heterometallic CuY_3 complex **1**. The reaction in the right stoichiometry improved the yield of the product [Equation (1)].

$$[Cu(TFA)_2(MeOH)] + 3\,[Y(TFA)_3(H_2O)_3] + 5\,mdeaH_2 \xrightarrow{thf} \underset{\mathbf{1}}{[CuY_3(\mu_3\text{-}OH)(mdeaH)_5(\eta^2\text{-}TFA)(\mu,\eta^2\text{-}TFA)_2](TFA)_2(H_2O)} + 6\,TFAH + 7\,H_2O \qquad (1)$$

In contrast, no heterometallic Y-Ba species was obtained by treating $[Y(TFA)_3(H_2O)_3]$ with $[Ba(TFA)_2]_\infty$, even in the presence of excess $mdeaH_2$. Instead, the 1D barium coordination polymer **2** was isolated and no yttrium derivative could be crystallised out. Complex **2**, which can also be obtained by treating $[Ba(TFA)_2]_\infty$ with 4/3 mol of $mdeaH_2$ in thf, is different from the previously reported Ba TFA derivatives with $mdeaH_2$ as ligand, namely the neutral complex $[Ba(TFA)_2(mdeaH_2)_2]$ (**3**)[12] or the ionic complex $[Ba(mdeaH_2)_3](TFA)_2$ (**4**; Scheme 1).[13]

Heterometallic Y(Ln)-Ba derivatives are quite scarce when compared to heterometallic Y(Ln)-Cu[4–8,15] or Ba-Cu[16] derivatives and are limited to compounds where the connection between the metals is ensured by classical[17] or fluorinated[18] alkoxides or siloxides.[19] Lanthanide–alkaline-earth metal heterometallic derivatives stabilized by hydroxyquinoline or aminocarboxylic acids are also known.[20]

Spectroscopic Characterisation

The FT-IR spectra of **1** and **2** show the presence of alcohol functionalities [ν(OH) absorptions at 3413 and 3330 for **1** and 3313 cm^{-1} for **2**] as well as trifluoroacetate groups in the metal coordination sphere. The $\nu_{as}(CO_2)$ absorption at high frequency (1698 cm^{-1}) suggests the presence of ionic TFA ligands, whereas that at 1660 cm^{-1} indicates a chelating-bridging TFA in **1**. The overlap of the $\nu_{as}(CO_2)$ absorptions due to the presence of different TFA ligands (monodentate, bidentate and bridging) in **2** results in a strong broad absorption centred at 1680 cm^{-1}. Strong C–F and C–O absorption bands in the 1120–1210 cm^{-1} range also characterise the spectra of **1** and **2**. Three characteristic absorptions for TFA derivatives are found in the 850–720 cm^{-1} region.[12–14] The low-frequency absorptions at 632–404 cm^{-1} are due to the ν(M–O) and ν(M–N) vibrations.[12–14] The ^1H NMR spectrum of **2** indicates the presence of protonated *N*-methyldiethanolamine ligands in at least two different environments. It exhibits a broad peak at $\delta = 5.30$ ppm, two triplets ($J = 6.0$ Hz) at $\delta = 3.85$ and 3.75 ppm, two broad peaks at $\delta = 2.82$ and 2.53 ppm and a singlet at $\delta = 1.86$ ppm due to OH, OCH_2, NCH_2 and NMe groups, respectively. The X-band ESR spectrum of polycrystalline **1** at room temperature exhibits a well-resolved hyperfine structure ($A_\parallel = 47$ G) due to interaction of the unpaired electron with the nuclear spin ($I = 3/2$) of both ^{63}Cu and ^{65}Cu (Figure 1). It reveals that the Cu^{II} centre is indeed axial ($2.0 < g_\perp < g_\parallel$) with a $d_{x^2-y^2}$ ground state. The

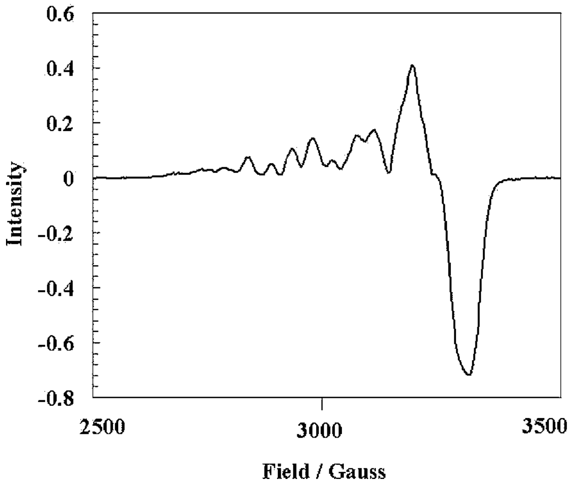
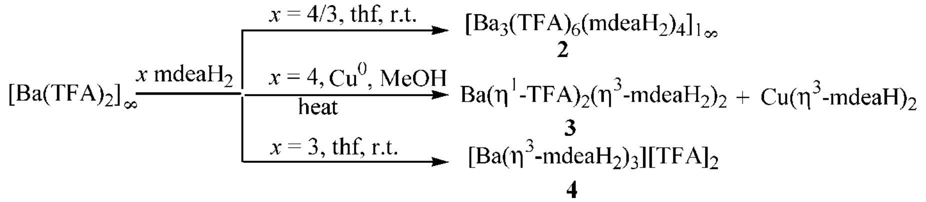


Figure 1. Room-temperature ESR spectrum of **1**.



Scheme 1. Reactions of $[Ba(TFA)_2]_\infty$ with $mdeaH_2$ with different stoichiometries and conditions.

values of the spin Hamiltonian parameters, $g_{\perp} = 2.047$ and $g_{\parallel} = 2.281$, are typical for a tetragonally distorted octahedral Cu^{II} ion.[21]

Molecular Structures of [CuY$_3$(μ_3-OH)(μ-η^3:η^1-mdeaH)$_3$(μ_3-η^3:η^1:η^1-mdeaH)$_2$(η^2-TFA)(μ,η^2-TFA)$_2$](TFA)$_2$(H$_2$O) (1) and [Ba$_3$(η^3-mdeaH$_2$)$_2$(μ-η^3:η^1-mdeaH$_2$)$_2$(η^1-TFA)$_2$(η^2-TFA)$_2$(μ_3-η^2:η^2:η^1-TFA)$_2$]$_{1\infty}$ (2)

A single-crystal X-ray diffraction study of [CuY$_3$(μ_3-OH)(μ-η^3:η^1-mdeaH)$_3$(μ_3-η^3:η^1:η^1-mdeaH)$_2$(η^2-TFA)(μ,η^2-TFA)$_2$](TFA)$_2$(H$_2$O) (**1**) revealed that it is an ionic complex (Figure 2, Table 1). All five amino alcohols are only partially deprotonated to afford mdeaH ligands. These are of two types, which act either in a doubly or triply bridging-chelating manner. The cationic species can be described as a regular triangular Y$_3$ unit [3.4805(6)–3.5503(6) Å] capped by oxygen atoms O10 and O6 of the mdeaH ligands. The Y atoms are eight-coordinate for Y1 and Y3 and nine-coordinate for Y2. Nine-coordinate yttrium atoms are rare in alkoxide chemistry, although they have been observed with poly(amino alkoxides).[22] The connection between yttrium atoms Y1, Y2 and the copper atom is achieved through oxygen atom O1M3, which is actually a hydroxide ligand, with a tetrahedral configuration, as well as by the oxygen atoms of two μ,η^2-trifluoroacetates and one deprotonated oxygen of an *N*-methylethanolaminate ligand. The third trifluoroacetate ligand is linked in a chelating manner to Y2. The six-coordinate copper atom has an O$_5$N environment where the Cu–O1 [2.549(4) Å] and Cu–O13 [2.453(4) Å] bond lengths are longer than the other Cu–O bond lengths (1.948 Å av.) as a combined result of the coordination with an alcohol functionality and a Jahn–Teller distortion.[23] The Cu–N1 bond length [2.028(4) Å] is in good agreement with those found in other copper complexes with N-heterocyclic ligands.[23] The Y–O bond lengths vary from 2.245(3)

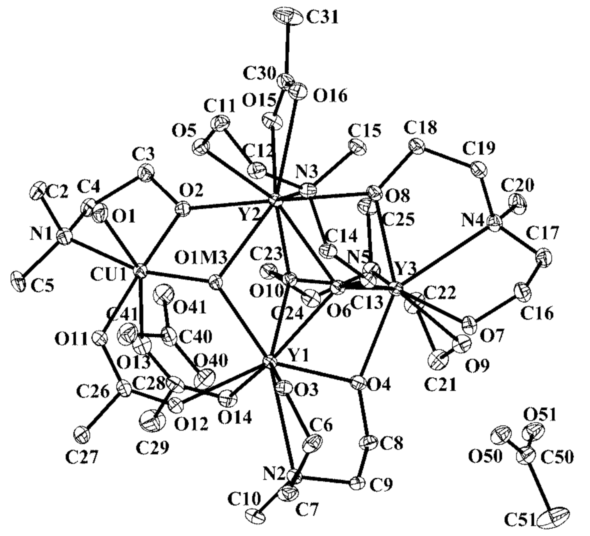


Figure 2. Molecular structure of **1** with atom labelling and ellipsoids at 30% probability. Hydrogen atoms have been omitted for clarity.

Table 1. Selected bond lengths [Å] and bond angles [°] for **1**.

Cu1–O2	1.906(3)	Cu1–O1M3	1.956(3)
Cu1–O11	1.983(3)	Cu1–N1	2.028(4)
Cu1–O13	2.453(4)	Cu1–O1	2.549(4)
Y3–O8	2.245(3)	Y3–O4	2.272(3)
Y3–O6	2.346(3)	Y3–O7	2.348(3)
Y3–O10	2.385(3)	Y3–O9	2.404(3)
Y3–N5	2.576(4)	Y3–N4	2.643(4)
Y3···Y1	3.4805(6)	Y3···Y2	3.5503(6)
Y2–O2	2.313(3)	Y2–O8	2.332(3)
Y2–O10	2.337(3)	Y2–O1M3	2.414(3)
Y2–O5	2.458(3)	Y2–O6	2.487(3)
Y2–O16	2.488(3)	Y2–O15	2.520(4)
Y2–N3	2.616(4)	Y1–O1M3	2.308(3)
Y1–O4	2.255(3)	Y1–O14	2.322(3)
Y1–O6	2.363(3)	Y1–O3	2.402(3)
Y1–O12	2.417(3)	Y1–O10	2.416(3)
Y1–N2	2.626(4)		
O2–Cu1–O1M3	84.2 (1)	O2–Cu1–O11	177.3(1)
O1M3–Cu1–O11	93.7(1)	O2–Cu1–N1	87.1(1)
O1M3–Cu1–N1	164.3(2)	O11–Cu1–N1	95.3(2)
O2–Cu1–O13	97.7(1)	O1M3–Cu1–O13	105.6(1)
O11–Cu1–O13	81.2(1)	N1–Cu1–O13	88.5 (2)
O2–Cu1–O1	100.1(1)	O1M3–Cu1–O1	88.8(1)
O11–Cu1–O1	81.6(1)	N1–Cu1–O1	79.9(2)
O13–Cu1–O1	158.2(1)	O8–Y3–O4	140.6(1)
O8–Y3–O6	71.2(1)	O4–Y3–O6	73.4(1)
O8–Y3–O7	109.4(1)	O4–Y3–O7	82.0(1)
O6–Y3–O7	82.3(1)	O8–Y3–O10	74.7(1)
O4–Y3–O10	74.2(1)	O6–Y3–O10	62.8(1)
O7–Y3–O10	142.0(1)	O8–Y3–O9	139.0(1)
O4–Y3–O9	79.7(1)	O6–Y3–O9	147.8(1)
O7–Y3–O9	76.7(1)	O10–Y3–O9	125.9(1)
O8–Y3–N5	92.1(1)	O4–Y3–N5	100.2(1)
O6–Y3–N5	133.7(1)	O7–Y3–N5	143.3(1)
O10–Y3–N5	71.3(1)	O9–Y3–N5	67.8(1)
O8–Y3–N4	69.7(1)	O4–Y3–N4	144.8(1)
O6–Y3–N4	117.6(1)	O7–Y3–N4	67.7(1)
O10–Y3–N4	141.0(1)	O9–Y3–N4	76.4(1)
N5–Y3–N4	94.2(1)	Y1···Y3···Y2	61.65(1)
O2–Y2–O8	135.6(1)	O2–Y2–O10	77.0(1)
O8–Y2–O10	74.0(1)	O2–Y2–O1M3	66.4(1)
O8–Y2–O1M3	133.4(1)	O10–Y2–O1M3	74.4(1)
O2–Y2–O5	71.1(1)	O8–Y2–O5	141.3(1)
O10–Y2–O5	144.3(1)	O1M3–Y2–O5	78.4(1)
O2–Y2–O6	124.2(1)	O8–Y2–O6	67.3(1)
O10–Y2–O6	61.4(1)	O1M3–Y2–O6	67.7(1)
O5–Y2–O6	126.9(1)	O2–Y2–O16	107.3(1)
O8–Y2–O16	76.7(1)	O10–Y2–O16	140.0(1)
O1M3–Y2–O16	144.7(1)	O5–Y2–O16	67.2(1)
O6–Y2–O16	128.5(1)	O2–Y2–O15	73.4(1)
O8–Y2–O15	75.8(1)	O10–Y2–O15	94.1(1)
O1M3–Y2–O15	139.7(1)	O5–Y2–O15	92.0(1)
O6–Y2–O15	139.9(1)	O16–Y2–O15	52.3(1)
O2–Y2–N3	132.5(1)	O8–Y2–N3	91.8(1)
O10–Y2–N3	130.0(1)	O1M3–Y2–N3	83.2(1)
O5–Y2–N3	67.5(1)	O6–Y2–N3	68.9(1)
O16–Y2–N3	77.0(1)	O15–Y2–N3	129.2(1)
Cu1···Y2···Y3	113.52(2)	O4–Y1–O1M3	140.9(1)
O4–Y1–O14	85.2(1)	O1M3–Y1–O14	111.6(1)
O4–Y1–O6	73.3(1)	O1M3–Y1–O6	71.5(1)
O14–Y1–O6	139.8(1)	O4–Y1–O3	104.9(1)
O1M3–Y1–O3	84.2(1)	O14–Y1–O3	141.2(1)
O6–Y1–O3	78.3(1)	O4–Y1–O12	143.8(1)
O1M3–Y1–O12	75.3(1)	O14–Y1–O12	75.7(1)
O6–Y1–O12	138.7(1)	O3–Y1–O12	74.6(1)
O4–Y1–O10	73.9(1)	O1M3–Y1–O10	74.9(1)
O14–Y1–O10	79.6(1)	O6–Y1–O10	62.1(1)
O3–Y1–O10	139.2(1)	O12–Y1–O10	130.3(1)
O4–Y1–N2	70.5(1)	O1M3–Y1–N2	144.6(1)
O14–Y1–N2	80.8(1)	O6–Y1–N2	120.9(1)
O3–Y1–N2	68.2(1)	O12–Y1–N2	76.2(1)
O10–Y1–N2	140.5(1)	Y3···Y1···Cu1	112.21(2)
Y3···Y1···Y2	60.13(1)	Cu1···Y1···Y2	57.02(1)
Cu1–O2–Y2	107.2(1)	Y1–O4–Y3	100.5(1)
Y3–O6–Y1	95.3(1)	Y3–O6–Y2	94.5(1)
Y1–O6–Y2	95.9(1)	Y3–O8–Y2	101.7(1)
Y2–O10–Y3	97.5(1)	Y2–O10–Y1	98.6(1)
Y3–O10–Y1	92.9(1)	Cu1–O1M3–Y1	111.4(1)
Cu1–O1M3–Y2	101.8(1)	Y1–O1M3–Y2	99.4(1)

to 2.520(3) Å, the order of variation being Y–O(μ,η^2-mdeaH) < Y–O(μ_3-OH) ≈ Y–O(μ_3,η^3-mdeaH) ≈ Y–O(η^1-mdeaH) ≈ Y–O(μ,η^2-TFA) < Y–O(η^2-TFA). The transannular Y–N bond lengths are longer (av. 2.615 Å) but are comparable to those reported for $[Y_2Cu_6(bdmap)_8(TFA)_{10}]$.[8] The distance between one TFA counteranion (O41) and the oxygen of the μ_3-hydroxo group O1M3···O41 is 2.802(6) Å, which suggests hydrogen bonding. The μ_3-OH must originate from the coordinated water of $[Y(TFA)_3(H_2O)_3]$ since **1** was obtained by treating $[Y(TFA)_3(H_2O)_3]$ with $[Cu(TFA)_2(MeOH)]$ and $mdeaH_2$ in anhydrous thf. This further confirms that the yttrium starting material is easily hydrolysed to form trinuclear Y_3 units.[14]

The structure of **2** is that of a homometallic Ba 1D coordination polymer of formula $[Ba_3(\eta^3\text{-}mdeaH_2)_2(\mu\text{-}\eta^3{:}\eta^1\text{-}mdeaH_2)_2(\eta^1\text{-}TFA)_2(\eta^2\text{-}TFA)_2(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^1\text{-}TFA)_2]_{1\infty}$. It contains two types of barium atoms, namely Ba1 and Ba2, which are present in a 2:1 ratio and form a zig-zag chain (Figures 3, 4 and 5). Selected bond lengths and angles are collected in Table 2. Polymer **2** can be seen formally as the association between $[Ba_2(\eta^3\text{-}mdeaH_2)_2(\mu\text{-}\eta^3{:}\eta^1\text{-}mdeaH_2)_2(\mu,\eta^2{:}\eta^1\text{-}TFA)_2]^{2+}$ and $[Ba(\eta^2\text{-}TFA)_2(\eta^1\text{-}TFA)_2]^{2-}$ units through one oxygen and one fluorine atom [Ba2···F = 3.010(3) Å] of $\mu,\eta^2{:}\eta^1$-TFA ligands, which overall act as unique triply bridging TFA ligands bonded in two different chelating manners [η^2(O,O) and η^2(O,F); Figures 3 and 4). The triply bridging μ_3-$\eta^1{:}\eta^2{:}\eta^1$ coordination mode is known for TFA (Scheme 2) for a Ba[24] and few other complexes,[25] but no secondary F···cation bond has been reported so far. Such metal–fluorine interactions appear to be a common feature for compounds of large elements such as alkaline-earth metals or lanthanides with fluorinated alkoxides or β-diketonates,[26] but are reported here for the first time with TFA.

Two types of amino alcohols coordinating to Ba1 are not deprotonated: one $mdeaH_2$ acts in a tridentate mode and

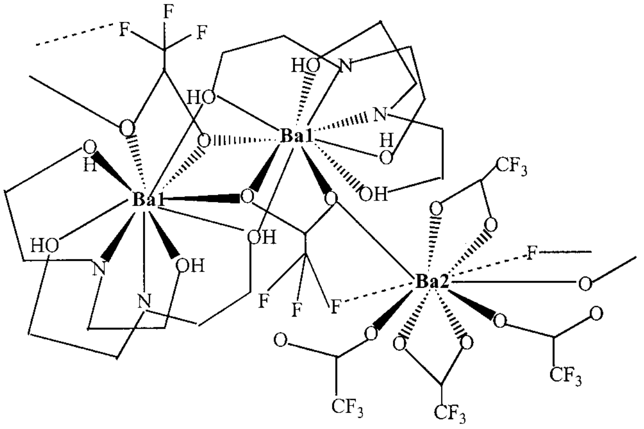


Figure 3. ChemDraw structure of $[Ba_3(\eta^3\text{-}mdeaH_2)_2(\mu\text{-}\eta^3{:}\eta^1\text{-}mdeaH_2)_2(\eta^1\text{-}TFA)_2(\eta^2\text{-}TFA)_2(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^1\text{-}TFA)_2]_{1\infty}$ (**2**).

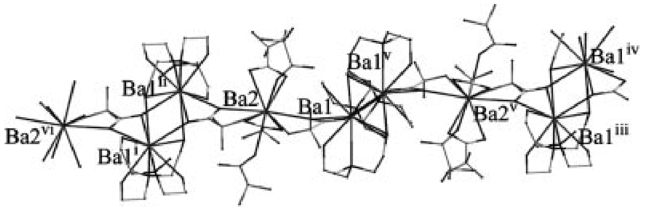


Figure 5. View of the 1D polymer chains of **2**. Symmetry elements: (i) $^1/_2 + x, ^1/_2 - y, ^1/_2 + z$; (ii) $2 - x, y, ^1/_2 - z$; (iii) $-^1/_2 + x, ^1/_2 - y, -^1/_2 + z$; (iv) $1 - x, y, -^1/_2 - z$; (v) $^3/_2 - x, ^1/_2 - y, -z$; (vi) $^5/_2 - x, ^1/_2 - y, 1 - z$.

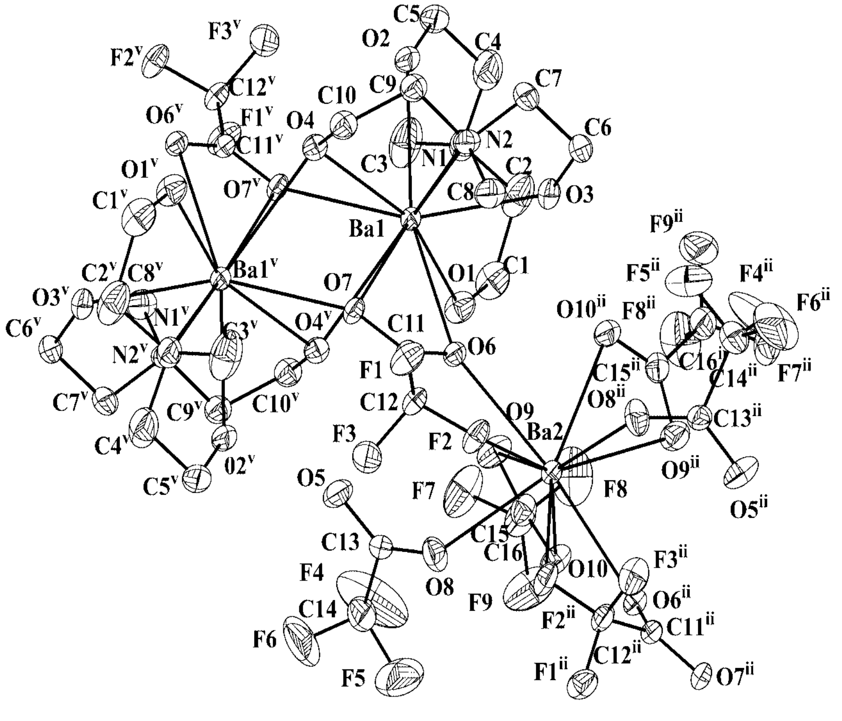


Figure 4. Molecular structure of **2** with atom labelling and ellipsoids at 30% probability. Hydrogen atoms have been omitted for clarity.

Table 2. Selected bond lengths [Å] and bond angles [°] for **2**.[a]

Ba1–O1	2.721(4)	Ba2–O8	2.668(4)
Ba1–O2	2.769(4)	Ba2–O8^{i}	2.668(4)
Ba1–O3	2.733(4)	Ba2–O9	2.833(4)
Ba1–O4	2.906(4)	Ba2–O9^{i}	2.833(4)
Ba1–O4^{ii}	2.929(4)	Ba2–O10	2.863(5)
Ba1–O6	2.952(3)	Ba2–O10^{i}	2.863(5)
Ba1–O7	3.064(4)	Ba1–N1	3.001(6)
Ba1–O7^{ii}	2.778(3)	Ba1–N2	3.034(5)
Ba2–O6	2.795(3)	Ba2–F2	3.010(3)
Ba2–O6^{i}	2.795(3)	Ba2–F2^{i}	3.010(3)
O1–Ba1–O3	79.952(1)	O4^{ii}–Ba1–O7	58.137(9)
O1–Ba1–O2	117.042(1)	O4^{ii}–Ba1–N1	133.874(1)
O1–Ba1–O7^{ii}	101.527(1)	O4^{ii}–Ba1–N2	78.129(1)
O1–Ba1–O4	160.582(1)	O6–Ba1–O7	43.667(9)
O1–Ba1–O4^{ii}	72.268(1)	O6–Ba1–N1	133.874(1)
O1–Ba1–O6	82.185(1)	O6–Ba1–N2	78.129(1)
O1–Ba1–O7	114.982(1)	N1–Ba1–N2	113.029(1)
O1–Ba1–N1	59.043(1)	N1–Ba1–O7	173.267(1)
O1–Ba1–N2	137.554(1)	N2–Ba1–O7	73.358(1)
O3–Ba1–O2	83.301(1)	O8^{i}–Ba2–O8	134.73(1)
O3–Ba1–O7^{ii}	156.180(9)	O8^{i}–Ba2–O6^{i}	79.106(1)
O3–Ba1–O4	119.412(1)	O8^{i}–Ba2–O6	93.776(1)
O3–Ba1–O4^{ii}	138.345(1)	O8^{i}–Ba2–O9^{i}	75.120(1)
O3–Ba1–O6	77.365(1)	O8^{i}–Ba2–O9	146.984(1)
O3–Ba1–O7	110.523(9)	O8^{i}–Ba2–O10	139.910(1)
O3–Ba1–N1	72.422(1)	O8^{i}–Ba2–O10^{i}	75.770(1)
O3–Ba1–N2	59.271(1)	O8–Ba2–O6^{i}	93.776(1)
O2–Ba1–O7^{ii}	74.823(1)	O8–Ba2–O6	79.106(1)
O2–Ba1–O4	69.989(9)	O8–Ba2–O9^{i}	146.984(1)
O2–Ba1–O4^{ii}	137.004(9)	O8–Ba2–O9	75.120(1)
O2–Ba1–O6	149.897(9)	O8–Ba2–O10	75.770(1)
O2–Ba1–O7	127.738(9)	O8–Ba2–O10^{i}	139.910(1)
O2–Ba1–N1	58.021(1)	O6^{i}–Ba2–O6	161.585(9)
O2–Ba1–N2	72.172(1)	O6^{i}–Ba2–O9^{i}	76.608(1)
O7^{ii}–Ba1–O4	61.621(9)	O6^{i}–Ba2–O9	118.261(1)
O7^{ii}–Ba1–O4^{ii}	62.230(9)	O6^{i}–Ba2–O10	72.525(1)
O7^{ii}–Ba1–O6	126.455(9)	O6^{i}–Ba2–O10^{i}	121.076(1)
O7^{ii}–Ba1–O7	90.603(9)	O6–Ba2–O9^{i}	118.261(1)
O7^{ii}–Ba1–N1	87.818(1)	O6–Ba2–O9	76.608(1)
O7^{ii}–Ba1–N2	120.435(1)	O6–Ba2–O10	121.076(1)
O4–Ba1–O4^{ii}	90.341(9)	O6–Ba2–O10^{i}	72.525(1)
O4–Ba1–O6	99.841(9)	O9^{i}–Ba2–O9	81.806(1)
O4–Ba1–O7	59.204(9)	O9^{i}–Ba2–O10	71.214(1)
O4–Ba1–N1	125.190(1)	O9^{i}–Ba2–O10^{i}	45.754(1)
O4–Ba1–N2	61.00(1)	O9–Ba2–O10	45.754(1)
O4^{ii}–Ba1–O6	68.744(9)	O9–Ba2–O10^{i}	71.214(1)
		O10–Ba2–O10^{i}	95.152(1)

[a] Symmetry codes: (i) $2 - x, y, {}^{1}/_{2} - z$; (ii) ${}^{3}/_{2} - x, {}^{1}/_{2} - y, - z$.

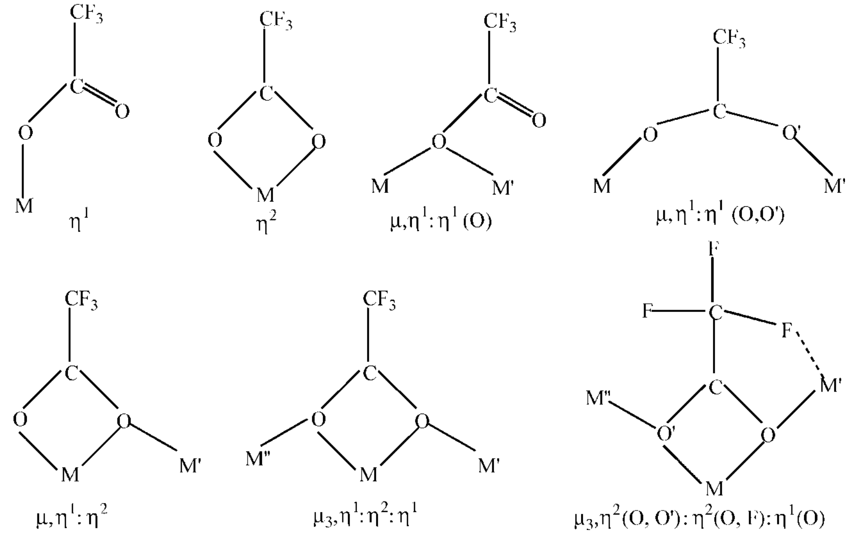
the other one acts as a bridging ligand with one OH as well as a tridentate ligand. The coordination number of 10 around each Ba1 is achieved by two η^3-mdeaH$_2$ ligands, one η^2-TFA [actually the triply bridging one bonded in an η^2(O,O) manner], one η^1-mdeaH$_2$ (bridging) and an η^1-TFA (actually the triply bridging one bonded in a μ-O manner). Two η^1-TFA, two η^2-TFA and two triply bridging TFA ligands bonded in an η^2(O,F) manner provide a coordination number of 10 around Ba2 as well. The Ba1···Ba1# distance is 4.115(9) Å, whereas the Ba1···Ba2 ones are longer [5.292(1) Å]. The Ba–O(μ-mdeaH$_2$) bond lengths [2.906(4)–2.929(4) Å] are longer than the terminal Ba–OH [2.721(4)–2.769(4) Å] one (Table 2). The Ba1–O(TFA) bond lengths vary from 2.779(4) to 3.064(4) Å. The transannular Ba–N coordination bond lengths [3.001(6)–3.034(5) Å] are comparable with those reported in [Ba(η^1-TFA)$_2$(mdeaH$_2$)$_2$].[12] The Ba2 atom bears two monodentate and two bidentate trifluoroacetate ligands. The Ba2–O(η^1-TFA) bond length [2.668(4) Å] is shorter than those for bidentate TFA [2.833(4)–2.863(5) Å] and bridging TFA [2.795(3)]. Compound **2** is the only example thus far where Ba is linked to both mono- and bidentate as well as bridging trifluoroacetate ligands.

The structure of **2** shows the versatility of the reactions between [Ba(TFA)$_2$]$_\infty$ and *N*-methyldiethanolamine (mdeaH$_2$) since it is the third Ba-TFA-mdeaH$_2$ derivative (Scheme 1). The two other derivatives have recently been reported by us.[12,13] The eight-coordinate Ba centre in [Ba(η^1-TFA)$_2$(mdeaH$_2$)$_2$] (**3**) bears two monodentate dangling trifluoroacetate and two *N*-methyldiethanolamine ligands,[12] whereas ionic [Ba(mdeaH$_2$)$_3$][TFA]$_2$ (**4**) has a nine-coordinate Ba^{2+} cation surrounded by three tridentate *N*-methyldiethanolamines, with two trifluoroacetate ligands acting as counterions.[13] No Ba···F short interactions are found in the solid. Strict control of the stoichiometry is required for access to a specific Ba-TFA adduct with the neutral mdeaH$_2$ ligand. The absence of deprotonation of amino alcohols in Ba-TFA adducts, probably due to the large radius of Ba^{2+} cation, precludes the formation of Y-Ba heterometallic complexes. In contrast, the reaction between Y and Cu TFA derivatives proceeds with partial deprotonation of amino alcohols and removal of some TFA as TFAH to form heterometallic compounds.

Experimental Section

All reactions were carried out under argon by using standard Schlenk-tube and vacuum-line techniques. Solvents were purified by standard methods. Trifluoroacetic acid (TFAH) was stored over molecular sieves. [Ba(TFA)$_2$], [Cu(TFA)$_2$(MeOH)][12,13] and [Y(TFA)$_3$(H$_2$O)$_3$][14] were prepared as reported previously. Analytical data were obtained from the Service Central d′Analyses du CNRS. FT-IR spectra were recorded as Nujol mulls with a Perkin–Elmer Paragon 500 spectrometer. NMR spectra were recorded with a Bruker AC-300 spectrometer. The ESR spectrum (X-band, 9.4 GHz) was obtained at room temp. for the powder with a Bruker spectrometer (microwave power of 10 mW, modulation frequency of 100 kHz). Diphenylpicrylhydrazyl (DPPH) was used as an internal reference (g = 2.0036).

Synthesis of [CuY$_3$(μ$_3$-OH)(mdeaH)$_5$(η^2-TFA)(μ,η^2-TFA)$_2$](TFA)$_2$(H$_2$O) (1): MeN(C$_2$H$_4$OH)$_2$ (0.5 mL, excess) was added dropwise to a greenish blue solution of [Cu(TFA)$_2$(MeOH)] (0.276 g, 0.85 mmol) and [Y(TFA)$_3$(H$_2$O)$_3$] (0.408 g, 0.85 mmol) in thf (20 mL). The colour of the solution changed to blue in a few minutes. After stirring overnight, blue crystals were obtained by layering the medium with Et$_2$O (0.29 g, 67% based on Y). The reaction in the right stoichiometry {[Cu(TFA)$_2$(MeOH)] (0.095 g, 0.26 mmol), [Y(TFA)$_3$(H$_2$O)$_3$] (0.381 g, 0.73 mmol), MeN(C$_2$H$_4$OH)$_2$ (0.5 mL, excess)} improved the yield of the product (0.31 g, 78%). C$_{35}$H$_{62}$CuF$_{15}$N$_5$O$_{22}$Y$_3$ (1520.1): calcd. C 27.65, H 4.11, N 4.61; found C 27.35, H 4.09, N 4.57. IR (nujol): $\tilde{\nu}$ = 3413 cm^{-1} w, 3330 m [ν(OH)]; 1698 s, 1660 m [ν$_{as}$(CO$_2$)], 1462 s [ν$_s$(CO$_2$)], 1213 s, 1195 s, 1139 s [ν(C–F)], 844 w, 800 m, 723 m, 632 w, 615 w, 597 w, 588 w, 557 w, 541 w, 521 w, 459 m.



Scheme 2. Various bonding modes observed in TFA complexes.

$[Ba_3(\eta^3\text{-mdeaH}_2)_2(\mu\text{-}\eta^3{:}\eta^1\text{-mdeaH}_2)_2(\eta^1\text{-TFA})_2(\eta^2\text{-TFA})_2(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^1\text{-TFA})_2]_{1\infty}$ (2): $MeN(CH_2CH_2OH)_2$ (0.5 mL, excess) was added to a solution of $[Y(TFA)_3(H_2O)_3]$ (0.88 g, 1.83 mmol) and $[Ba(TFA)_2]$ (0.67 g, 1.84 mmol) in thf (20 mL) and the medium was stirred overnight. Colourless needles (0.81 g, 84% based on Ba) were obtained at room temp. by concentration (3 mL). Anal: found (calcd.) for $C_{32}H_{52}Ba_3F_{18}N_4O_{20}$ (1566.76): calcd. C 24.50, H 3.31, N 3.57; found C 24.39, H 3.27, N 3.56. IR (nujol): $\tilde{\nu}$ = 3313 cm^{-1} br [ν(OH)], 1670 s [$\nu_{as}(CO_2)$], 1461 s [$\nu_s(CO_2)$], 1194 s, 1130 s [ν(C–F)], 836 s, 787 s, 763 m, 714 s, 598 m, 512 m, 404 m. ^1H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 5.30 (br., 8 H, OH), 3.85, 3.75 (t, J = 6.0 Hz, 16 H, OCH_2), 2.82, 2.53 (br., 16 H, NCH_2), 1.86 ppm (s, 12 H, NMe). Compounds **1** and **2** are soluble in thf but insoluble in toluene, *n*-hexane and diethyl ether. Unlike **2**, which is moderately soluble in chloroform and dichloromethane, **1** is completely insoluble in these solvents.

Crystallography: Suitable crystals of **1** were obtained by layering its thf solution with Et_2O whereas a concentrated thf solution of **2** gave crystals at room temp. suitable for X-ray crystallography. X-ray single-crystal diffraction data were collected with a Nonius Kappa CCD diffractometer (λ = 0.71073 Å) using the COLLECT software (Nonius BV, 1997–2000) and processed with the DENZO reduction software.[27] The structure of **1** was solved and refined on F^2 using SHELXTL[28] whereas **2** was solved with the SIR97 program[29] and refined with CRYSTALS.[30] All non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were included in the final refinement in calculated positions with isotropic thermal parameters. Crystal data for $C_{35}H_{62}CuF_{15}N_5O_{22}Y_3$ (**1**): M_w = 1520.17, T = 163(2) K, triclinic, $P\bar{1}$, a = 12.646(2), b = 15.100(3), c = 15.793(3) Å, α = 104.134(1)°, β = 90.185(1)°, γ = 96.564(1)°, V = 2903.68(9) $Å^3$, Z = 2, $\mu(\text{Mo-}K_\alpha)$ = 3.451 mm^{-1}, reflections collected 24438, independent reflections 13214 [R(int) = 0.043], data/restraints/parameters 13214/0/766, R [$F^2 > 2\sigma(F^2)$] = 0.055, wR (F^2) = 0.150, R (all data) = 0.078, wR (all data) = 0.168, GOF = 1.17, residual electron density: –0.996 and 1.424 $e Å^{-3}$.

$C_{32}H_{52}Ba_3F_{18}N_4O_{20}$ (**2**): M_w = 1566.76, T = 150(2) K, monoclinic, $C2/c$, a = 17.008(5), b = 18.376(5), c = 17.659(5) Å, β = 92.436(5), V = 5514(3) $Å^3$, Z = 4, $\mu(\text{Mo-}K_\alpha)$ = 2.25 mm^{-1}, reflections collected 8528, independent reflections 8324 [R(int) = 0.069], data/restraints/parameters 5887/6/348, R [$F^2>2\sigma(F^2)$] = 0.056, $wR(F^2)$ = 0.060, R (all) = 0.087, wR (all data) = 0.076, GOF 1.08, residual electron density: –1.01 and 1.57 $e Å^{-3}$.

CCDC-244549 (for **1**) and -296883 (for **2**) 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.

Acknowledgments

The authors are grateful to the Region Rhone Alpes for financial support (Project Superflex) and a postdoctoral fellowship to S. M.

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Received: September 6, 2006