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Rational Syntheses, Structure, and Properties of the First Bismuth(II) Carboxylate

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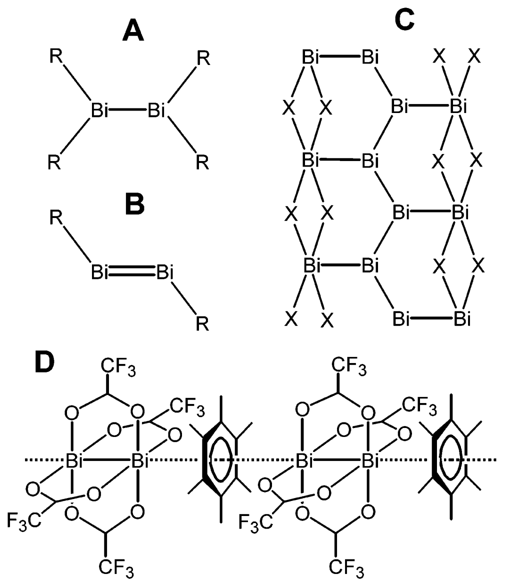
Bismuth(II) trifluoroacetate (**1**), the first inorganic salt of bismuth in oxidation state +2, has been obtained in its pure, unstabilized form. Several synthetic routes suggested for the isolation of the new compound include (i) mild oxidation of elemental bismuth with some metal trifluoroacetates, e.g., Ag^{I} and Hg^{II}; (ii) mild reduction of bismuth(III) trifluoroacetate with metals, such as Zn; (iii) comproportionation reaction between Bi and $Bi(O_2CCF_3)_3$. The last approach gives the title compound **1** in quantitative yield as a sole product. Bismuth(II) trifluoroacetate has been characterized by NMR, IR, and UV–vis spectroscopy as well as by single-crystal X-ray diffraction. Crystallographic study reveals the dinuclear paddle-wheel structure for diamagnetic molecules $Bi_2(O_2CCF_3)_4$. The Bi–Bi bond distances in dimetal units of **1** are averaged to 2.9462(3) Å, and there are no axial intermolecular contacts between these units in the solid state. The compound is volatile and exists in vapor phase up to 220 °C when it disproportionates back to Bi^0 and Bi^{III} species, i.e., by the reverse of the synthetic route iii. In contrast, the solution chemistry is quite limited: the bismuth(II) trifluoroacetate is decomposed by the majority of common solvents, but it can be stabilized by aromatic systems. The dibismuth unit has been shown to be preserved in the latter solvents and can be crystallized out in a form of π-adducts with arenes. Two such adducts, $Bi_2(O_2CCF_3)_4 \cdot (C_6H_5Me)$ (**2**) and $Bi_2(O_2CCF_3)_4 \cdot (1,4\text{-}C_6H_4Me_2)_2$ (**3**), have been isolated as single crystals and characterized by X-ray diffraction techniques. In the structures of both **2** and **3**, the bismuth(II) centers exhibit weak η^6-coordination to aromatic rings.

Chart 1



Introduction

Low-valent dibismuth organometallic compounds (Chart 1, **A** and **B**) can be synthesized in solution by reduction of Bi(III) species with alkali metals,[1] lithium alumohydride,[2] or cobaltocene.[3] On the other hand, binary inorganic compounds with homonuclear Bi–Bi bonds can be obtained in the solid state by reduction of bismuth(III) salts with metallic bismuth. The latter technique has been successfully applied for the isolation of various bismuth subhalides Bi_mX_n (m:n = 6:7, X = Cl,[4] Br;[5] 4:4 (**C**), X = Br,[5] I;[6] 14:4,[7] 18:4,[8] X = I). We attempted to extend this synthetic approach for

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the preparation of other classes of low-valent bismuth compounds, in particular for carboxylates. Reduced bismuth carboxylates were unknown until recently,[9] when Frank et al. demonstrated that bismuth(II) trifluoroacetate exists, at least in the vapor phase, and may be stabilized in the form of a one-dimensional coordination copolymer with hexamethylbenzene (**D**). Here we report for the first time several synthetic approaches to bismuth(II) trifluoroacetate (**1**) in pure, unstabilized form. The title compound has been obtained in the solid state in quantitative yield and fully characterized by NMR, UV−vis, and IR spectroscopy as well as by single-crystal X-ray diffraction.

Experimental Section

General Data. All of the manipulations were carried out in a dry, oxygen-free, dinitrogen or argon atmosphere by employing standard ampule and Schlenk techniques. Bismuth powder (99.99+%), zinc powder, bismuth(III) oxide, mercury(II) trifluoroacetate, and silver(I) trifluoroacetate were purchased from Aldrich and used as received. Bismuth(III) trifluoroacetate was prepared in 82% yield according to the literature procedure[10] and dried under vacuum for 24 h at room temperature and then for 48 h at 70 °C. UV−vis spectra were acquired using a Hewlett-Packard 8452A diode array spectrophotometer. IR spectra were recorded on a Nicolet Magna 550 FTIR spectrometer using KBr pellets and on a Perkin-Elmer spectrum RX I FT-IR system in chloroform solution. NMR spectra were obtained using a Varian Gemini 300 spectrometer at 282.2 MHz for ^{19}F and 75.4 MHz for ^{13}C. Chemical shifts are reported in ppm relative to TMS for ^{13}C and $CFCl_3$ for ^{19}F. All ^{13}C and ^{19}F NMR spectra were acquired in the proton-decoupled mode. X-band ESR measurements were recorded both on solid samples and in toluene solution at room temperature with a frequency of 9.4 GHz on an IBM-200D-SRC ESR spectrometer. Cyclic voltammograms were performed with a computer controlled CHI-620A (CH Instruments) in nitrogen-saturated CH_2Cl_2 solutions with tetrabutylammonium hexafluorophosphate (TBAH, 0.1 mol) as a supporting electrolyte.

Syntheses. Reaction of $Bi(O_2CCF_3)_3$ with Bi. A stoichiometric mixture of finely divided bismuth (0.021 g, 0.10 mmol) and bismuth(III) trifluoroacetate (0.109 g, 0.20 mmol) was sealed in an evacuated glass ampule. The container was then placed in an electric furnace having a temperature gradient along the length of the tube. The ampule was kept at 110 °C for 2 days to allow orange (red when heated) crystals of **1** to be quantitatively deposited in the coldest end of the tube where the temperature was set ca. 6−7 °C lower. UV−vis (C_7H_8, 22 °C) λ_{max}, nm (ϵ, $M^{-1}\cdot cm^{-1}$): 282 (sh, 970), 296 (1893), 422 (br., 657). UV−vis ($CHCl_3$, 22 °C) λ_{max}, nm (ϵ, $M^{-1}\cdot cm^{-1}$): 246 (2234), 270 (2471), 350 (sh, 526), 388 (1086). ^{19}F NMR (C_7D_8, 22 °C): δ −74.73 (s, CF_3), (CD_2Cl_2, 22 °C): δ −73.24 (s, CF_3). ^{13}C NMR (C_7D_8, 22 °C): δ 113.1 (q, J_{CF} = 284.9 Hz, CF_3), 175.4 (q, J_{CF} = 40.3 Hz, OCO). IR (KBr, cm^{-1}): 1668s, 1645s, 1435m, 1187s, 1153s, 846m, 792m, 726s, 522m. IR ($CHCl_3$, cm^{-1}): 1660s, 1644s, 1443m, 1190s, 1156s, 849w, 793w, 726m. The cyclic voltammogram of **1** in CH_2Cl_2 exhibits a series of irreversible redox couples at $E_{1/2}$ = +0.41, +1.15, −0.61, and −0.86 V. +ESI-MS ($CHCl_3$, m/z) 757 ($[Bi_2(O_2CCF_3)_3]^+$).

Reaction of $Bi(O_2CCF_3)_3$ with Zn. A mixture of bismuth(III) trifluoroacetate (0.055 g, 0.10 mmol) and activated zinc (0.020 g, 0.31 mmol) was evacuated and sealed in a glass ampule. A few orange crystals of **1** could be seen in the cold zone after the ampule was heated at 105 °C for 2 days.

Reaction of Bi with $Ag(O_2CCF_3)$. Bismuth powder (0.021 g, 0.10 mmol) and silver(I) trifluoroacetate (0.044 g, 0.20 mmol) were sealed in an evacuated Pyrex ampule and placed in a furnace at a temperature of 110 °C in the reaction zone. Crystals of **1** were formed in the cold and middle sections of the container. The yield after 4 days was ca. 40%. A silver mirror was also observed in the ampule.

Reaction of Bi with $Hg(O_2CCF_3)_2$. A mixture of metallic bismuth (0.042 g, 0.20 mmol) and mercury(II) trifluoroacetate (0.085 g, 0.20 mmol) was sealed under vacuum in a glass ampule. The reaction conditions were as those in the previous procedure with $Ag(O_2CCF_3)$. Orange crystals of **1** appeared in the cold zone of the tube along with drops of metallic mercury. The yield was about 70% (collected) after 4 days.

Crystal Growth. Crystals of the toluene adduct (**2**) were obtained by dissolving compound **1** (5 mg) in neat toluene (1 mL). A sealed NMR tube with yellow solution was placed in the freezer at −50 °C. Orange crystals of **2** accumulated at the bottom of the tube after 3 days. When open in air the crystals tend to lose solvent followed by their decomposition. Orange crystals of *p*-xylene adduct (**3**) were grown by a similar approach in the refrigerator at a temperature of ca. 10 °C.

X-ray Crystallographic Procedures. A single crystal of **1** selected from the solid state reaction of $Bi(O_2CCF_3)_3$ with Bi was used for structural determination. Crystals of **2** and **3** were obtained as described above. The X-ray intensity data were measured for **1** at 90(2) and 173(2) K and for **2** and **3** at 173(2) K (Bruker KRYO-FLEX) on a Bruker SMART APEX CCD-based X-ray diffractometer system equipped with a Mo-target X-ray tube (λ = 0.71073 Å) operated at 1800 W power. The crystals were mounted on a goniometer head with silicone grease. The detector was placed at a distance of 6.140 cm from the crystal. For each experiment a total of 1850 frames were collected with a scan width of 0.3° in ω and an exposure time of 20 s/frame. The frames were integrated with the Bruker SAINT software package using a narrow-frame integration algorithm to a maximum 2θ angle of 56.54° (0.75 Å resolution). The final cell constants are based upon the refinement of the *XYZ*-centroids of several thousand reflections above $20\sigma(I)$. Analysis of the data showed negligible decay during data collection. Data were corrected for absorption effects using the empirical method (SADABS).

The structures were solved and refined by full-matrix least-squares procedures on $|F^2|$ using the Bruker SHELXTL (version 6.12) software package. The coordinates of bismuth atoms for the structures were found in direct method *E* maps. The remaining atoms were located after an alternative series of least-squares cycles and difference Fourier maps. Aromatic hydrogen atoms in **3** were located and refined independently. All other hydrogen atoms were included in idealized positions for structure factor calculations. In the structure of **2** the methyl group of toluene was found to be disordered in two opposite directions. The fluorine atoms of most of the CF_3 groups in experiments at 173 K appeared to be disordered over three rotational orientations. No disorder of trifluoromethyl

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Table 1. Crystallographic Data for $Bi_2(O_2CCF_3)_4$ (**1**), $[Bi_2(O_2CCF_3)_4{\cdot}(C_6H_5Me)]_\infty$ (**2**), and $Bi_2(O_2CCF_3)_4{\cdot}(1,4\text{-}C_6H_4Me_2)_2$ (**3**)

	1	2	3
formula	$Bi_2O_8C_8F_{12}$	$Bi_2O_8C_{15}F_{12}H_8$	$Bi_2O_8C_{24}F_{12}H_{20}$
fw	870.04	962.17	1082.36
crystal system	monoclinic	monoclinic	triclinic
space group	$P2_1/n$	$C2/c$	$P\bar{1}$
a (Å)	8.1792(6)	11.8730(9)	9.0356(5)
b (Å)	14.8836(12)	14.4229(10)	9.6154(6)
c (Å)	21.7639(17)	13.7818(10)	9.9363(6)
β (deg)	98.4100(10)	90.4510(10)	78.1150(10)
V (Å^3)	2621.0(4)	2360.0(3)	821.42(8)
Z	6	4	1
ρ_{calcd} (g·cm^3)	3.307	2.708	2.188
μ (mm^{-1})	20.276	15.027	10.806
radiation (λ, Å)	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)
transm factors	0.1065−0.2938	0.1972−0.2657	0.2211−0.6718
temp (K)	90(2)	173(2)	173(2)
data/restraints/params	6141/ 0/406	2779/ 36/196	3684/ 18/235
$R1$,[a] w$R2$[b]			
$I > 2\sigma(I)$	0.0236, 0.0560	0.0481, 0.0881	0.0230, 0.0544
all data	0.0286, 0.0575	0.0549, 0.0903	0.0258, 0.0554
quality-of-fit[c]	1.042	1.232	1.045

[a] $R1 = \sum||F_o| - |F_c|/\sum|F_o|$. [b] $wR2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$. [c] Quality-of-fit $= [\sum[w(F_o^2 - F_c^2)^2]/(N_{obs} - N_{params})]^{1/2}$, based on all data.

groups was encountered in the structure of **1** at 90 K. Anisotropic displacement parameters were assigned to all non-hydrogen atoms, except the disordered fluorines. Relevant crystallographic data for all compounds are summarized in Table 1. Selected bond lengths and angles are given in Table 2.

Results and Discussion

Synthesis. In general, bismuth(II) trifluoroacetate (**1**) can be obtained either by mild reduction of bismuth(III) trifluoroacetate or by mild oxidation of metallic bismuth with metal trifluoroacetates. The title compound has been synthesized in quantitative yield as the only product of the comproportionation reaction:

$$Bi + 2Bi(O_2CCF_3)_3 \rightarrow 3\ Bi(O_2CCF_3)_2 \qquad (1)$$

The reaction was carried out in a sealed Pyrex ampule at 110 °C, and the product **1** was deposited in the cold zone of the tube in the form of large prismatic orange crystals. The completion of the reaction and mass transfer takes about 2 days, and the product may be collected in pure form, free of any impurities. This process is very similar to the preparation of crystalline bismuth subhalides[5−8] Bi_nX_4 ($X = Br$, $n = 4$; $X = I$, $n = 4, 14, 18$), but it requires lower temperatures due to higher volatility of the trifluoroacetate compared to the subhalides.

We have also attempted the reduction of $Bi(O_2CCF_3)_3$ by metallic bismuth in refluxing toluene solution, but did not observe any color change indicative of a reaction even after several days. Activated zinc can be used instead of metallic bismuth to provide the reductive power for bismuth(III) trifluoroacetate in the solid state. However, the yield of **1** was far from quantitative in this case. In addition, there was a problem of separation of the product from zinc trifluoroacetate. As an alternative approach, we have demonstrated that metallic bismuth can be mildly oxidized to Bi^{II} by 2 equiv of silver(I) trifluoroacetate with 40% yield:

$$Bi + 2Ag(O_2CCF_3) \rightarrow Bi(O_2CCF_3)_2 + 2Ag \qquad (2)$$

Similarly, an equimolar amount of mercury(II) trifluoroacetate can be used for the preparation of **1** from elemental bismuth:

$$Bi + Hg(O_2CCF_3)_2 \rightarrow Bi(O_2CCF_3)_2 + Hg \qquad (3)$$

The yield of **1** in this reaction is relatively high; however, the required separation from mercury makes this method less advantageous than comproportionation process 1.

Bismuth(II) trifluoroacetate has been obtained previously[9] only in a form of coordination copolymer with hexamethylbenzene in low (ca. 20%) yield by an unclarified thermolysis of bismuth(III) trifluoroacetate in the presence of arene. In that case, either the partial reduction of $Bi(O_2CCF_3)_3$ by C_6Me_6 takes place or disproportionation of Bi^{III} to Bi^{II} and higher oxidation states of bismuth (Bi^{IV} and/or Bi^{V}) occurs. In our attempts to clarify the mechanism of the above reaction, the arene complex of **1** was always a minor product (<10%). The major product was always an unreduced Bi^{III} trifluoroacetate coordination complex with hexamethylbenzene. Some of our observations support the idea of at least partial thermal disproportionation of $Bi(O_2CCF_3)_3$. Thus, when neat Bi^{III} trifluoroacetate is heated at 110 °C in a sealed vessel, a few orange blocks of **1** can be detected in the cold section of the tube along with small colorless crystals.

Properties. Bismuth(II) trifluoroacetate is highly volatile and starts to sublime at about 60 °C. It shows fair thermal stability in a sealed ampule until it decomposes back to bismuth(0) and Bi^{III} trifluoroacetate around 220 °C. It is worth noting that decomposition of **1** takes place in the vapor phase and produces well-shaped rhombohedral crystals of metallic bismuth in different parts of the ampule. In open air, the crystals of **1** immediately turn red and rapidly degrade, leaving a colorless liquid containing fine black powder (metallic bismuth). Bismuth(II) trifluoroacetate is

Table 2. Selected Bond Lengths (Å) and Angles (deg) for $Bi_2(O_2CCF_3)_4$ (**1**), $[Bi_2(O_2CCF_3)_4{\cdot}(C_6H_5Me)]_\infty$ (**2**), $Bi_2(O_2CCF_3)_4{\cdot}(1,4\text{-}C_6H_4Me_2)_2$ (**3**), and $[Bi_2(O_2CCF_3)_4{\cdot}(C_6Me_6)]_\infty$ (**4**)

	1	2	3	4[c]
Bi−Bi	2.9516(3),[a] 2.9407(3)[b]	2.9395(6)	2.9635(3)	2.9466(11)
Bi−O	2.378(4)−2.409(3)[a] 2.348(4)−2.432(4)[b]	2.375(7)−2.404(8)	2.380(3)−2.416(3)	2.387(6)−2.417(7)
Bi···C		3.427(10)−3.537(9)	3.307(5)−3.464(5)	3.354(4)−3.358(3)
Bi−Bi−O[d]	81.47(8)	81.6(2)	81.35(8)	81.4(2)
O−Bi−O[d]	88.74(14), 163.12(12)	88.9(3), 163.1(2)	88.70(13), 162.64(11)	88.8(3), 162.8(4)

[a] For centrosymmetric molecule. [b] For noncentrosymmetric molecule. [c] From ref 9. [d] Averaged values.

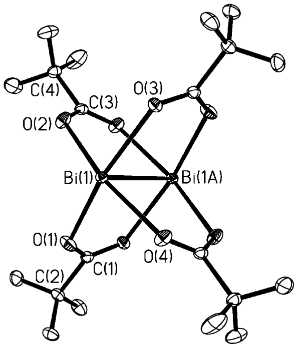


Figure 1. A perspective drawing of a centrosymmetric molecule in the crystal structure of bismuth(II) trifluoroacetate (**1**). Atoms are represented by thermal ellipsoids at the 40% probability level.

soluble in anhydrous, deoxygenated benzene, xylene, and toluene and can be kept in the latter solvent for a long time, especially at low temperatures. Traces of water obviously initiate the disproportionation of **1**, even in aromatic solvents, which can be followed by UV−vis observations. Compound **1** is also soluble in dichloromethane and chloroform, but cannot be preserved in these solvents for more than several minutes. The color of the solutions gradually turns pale, and traces of precipitating bismuth can be seen. The crystals of **1** are practically insoluble in hexanes and pyridine, while they are immediately decomposed by a majority of common solvents, such as THF, ether, acetone, alcohols, acetonitrile, and water. It is so sensitive toward these solvents that even handling the compound in dinitrogen or argon gloveboxes requires the absence of any solvent vapors.

Structure. The structure of **1** consists of two crystallographically independent dimetal tetrabridged $Bi_2(O_2CCF_3)_4$ units located in the unit cell at an angle of 74° to each other. Only one of these units resides on an inversion center. Bismuth(II) trifluoroacetate in its pure form indeed maintains a paddle-wheel structure (Figure 1) similar to the one that has been observed[9] in its coordination copolymer with hexamethylbenzene. This behavior is in contrast to what we have recently reported[11] for mercury(II) trifluoroacetate that reveals dimeric tetrabridged structure in the complex $[Hg_2(O_2CCF_3)_4 \cdot C_6Me_6]_\infty$,[12] but which exhibits a very complex layered network built on monomeric $Hg(O_2CCF_3)_2$ units in its unligated form. The major structural feature of **1** is the total absence of any kind of axial interactions between dibismuth units (Figure 2). Each bismuth atom maintains a slightly distorted square pyramidal coordination composed of one Bi and four O atoms. The closest contacts to the open coordination site on bismuth are fluorine atoms from neighboring units at distances of longer than 3.3 Å. The presence of discrete dibismuth units makes the bismuth(II) trifluoroacetate structure unique among other dimetal(II) tetra(trifluoroacetates) bearing no exogenous ligands. The latter are known[13−16] to maintain a 1D polymeric structure (Chart 2) due to axial coordination of the metal center to a carboxylate oxygen of a neighboring unit (Table 3).

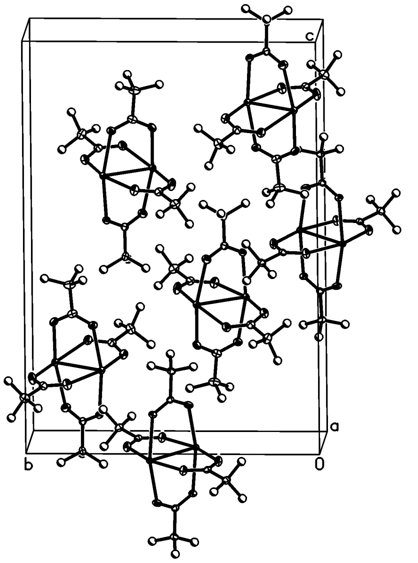
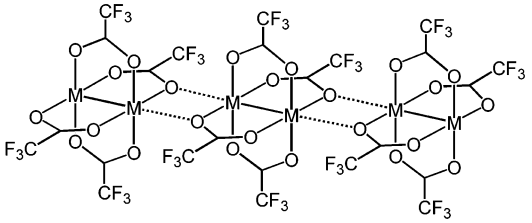


Figure 2. Packing diagram showing six discrete molecules of $Bi_2(O_2CCF_3)_4$ in the unit cell of the structure **1**.

Chart 2



There is a single bond between two bismuth atoms in **1** in accord with the fact that it is diamagnetic in the solid state. The bismuth−bismuth distances are 2.9516(3) Å and 2.9407(3) Å for centrosymmetric and noncentrosymmetric units, respectively. The Bi−Bi bond has almost the same length as that in the bismuth(II) trifluoroacetate complexes with hexamethylbenzene,[9] toluene, and xylene (Table 4). The shortening effect of bridging ligands can be clearly seen when we compare the Bi−Bi bond in **1** with those in nonbridged dibismuth organometallic compounds Bi_2R_4 (2.983−3.053 Å, Table 4) and in metallic bismuth.[17] On the other hand, the Bi−Bi bonding in **1** is longer than a double Bi═Bi bond found in Bi^{I} organometallic compounds Bi_2R_2 with bulky R-substituents, as well as in the "naked" Bi_2^{2-} anion.[18]

Bismuth(II) trifluoroacetate does not exhibit any phase transition during cooling down to −183 °C. The crystals of

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Table 3. Characteristic Structural Parameters for Dimetal(II) Tetra(trifluoroacetates)

metal	M−M (Å)	bond	M−O (Å)	M−M−O (deg)	M···O (Å)	M−M···O (deg)	ref
Bi	2.9462(3)	single	2.386(4)	81.47(8)			this work
Mo	2.090(4)	quadruple	2.057(8)	92.1(2)	2.72(1)	161.0(2)	13
Ru	2.2645(6)	double	2.066(3)	89.63(9)	2.375(3)	167.49(8)	14
Rh	2.3813(8)	single	2.047(3)	88.2(1)	2.337(4)	169.3(1)	15
Cu[a]	3.086(2)	none	1.922(6), 2.419(5)	67.4(1)−92.0(2)	2.054(5)	143.8(2)	16

[a] $Cu_2(O_2CCF_3)_4$ maintains a different structure with intermolecular Cu−O interactions being short and one of the intramolecular Cu−O contacts being long.

Table 4. The Bi−Bi Bond Lengths in Dibismuth Complexes

complex	Bi−Bi (Å)	ref
$Bi_2(O_2CCF_3)_4$	2.9407(3), 2.9516(3)	this work
$Bi_2(O_2CCF_3)_4 \cdot C_6H_5Me$	2.9395(6)	this work
$Bi_2(O_2CCF_3)_4 \cdot C_6Me_6$	2.947(1)	9
$Bi_2(O_2CCF_3)_4 \cdot (1,4\text{-}C_6H_4Me_2)_2$	2.9635(3)	this work
$[Bi_2Et_4][AlBu^t_3]_2$	2.983(1)	19a
$[Bi_2Et_4][GaBu^t_3]_2$	2.984(1)	19a
Bi_2Ph_4	2.984(2), 2.988(1), 2.990(2)	1c,d, 19c
Bi_2(2,2′,5,5′-tetramethyldibismole)	2.990(2)	1a
$Bi_2(SiMe_3)_4$	3.035(3)	19b
$Bi_2[CH(SiMe_3)_2]_4$	3.053(1)	2
$Bi_2[Ge(C_6F_5)_2]_4$	3.045(3)	19d
α-Bi (metal)	3.072	17
$Bi_2(2,6\text{-}Mes_2H_3C_6)_2$	2.8327(14)	1b
Bi_2Tbt_2[a]	2.8206(8)	18a
Bi_2Bbt_2[b]	2.8699(6)	18b
Bi_2^{2-}	2.8377(7)	18c

[a] Tbt = 2,4,6-$[(Me_3Si)_2CH]_3C_6H_2$. [b] Bbt = 2,6-$[(Me_3Si)_2CH]_2$-4-$[(Me_3Si)_3C]C_6H_2$.

1 show relatively high thermal compressibility: 1.9 vol % on going from −100 to −183 °C. That behavior is similar to that of some other metal trifluoroacetates; e.g., ruthenium(II) trifluoroacetate shrinks 1.9% in the same temperature range. Such "shrinkage" might be attributed to the changes in orientational disorder of carboxylate CF_3 groups. While trifluoromethyl groups are severely disordered at higher temperatures, this disorder essentially disappears at lower temperatures, allowing the dimetal units to come closer to each other.

Compound **1** was found to be diamagnetic, and no ESR signals were observed at room temperature in toluene solution, thus suggesting no tendency for Bi−Bi bond cleavage under these conditions. Bismuth(II) trifluoroacetate can be crystallized from toluene solution in a form of 1:1 coordination copolymer (**2**). The structure consists of infinite chains $[Bi_2(O_2CCF_3)_4 \cdot (C_6H_5Me)]_\infty$ (Figure 3) running in two almost perpendicular directions within the unit cell. The coordination of bismuth to aromatic rings in **2** can be described as η^6 (Table 2) with the distance from metal to the center of the ring being 3.23 Å. The aromatic planes, however, are not perpendicular to the Bi−Bi vector, with the angle between the latter and the normal to the plane being 18.5°.

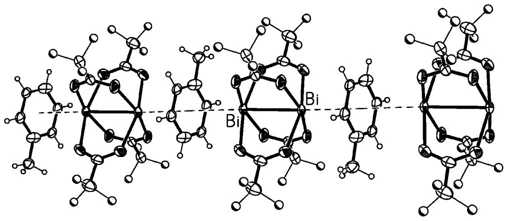

Figure 3. A fragment showing the alternating arrangement of $Bi_2(O_2CCF_3)_4$ and toluene molecules in the chain structure of monoadduct **2**. Only one orientation of the disordered CF_3 and CH_3 groups is depicted.

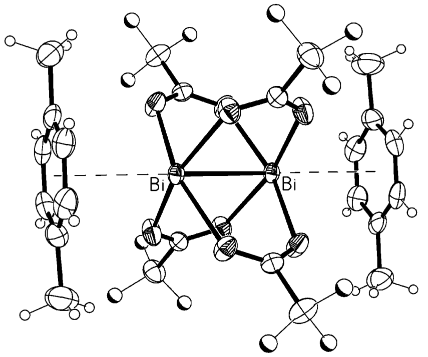

Figure 4. A perspective drawing of the $Bi_2(O_2CCF_3)_4$ bis-adduct with *p*-xylene (**3**). Fluorine and hydrogen atoms are shown as spheres of arbitrary radii. Only bismuth atoms are labeled for clarity.

From solution of **1** in neat *p*-xylene, yet a different type of adduct, $Bi_2(O_2CCF_3)_4 \cdot (1,4\text{-}C_6H_4Me_2)_2$ (**3**), has been crystallized. Bis-adduct **3** exhibits a discrete structure (Figure 4) with the dibismuth unit flanked by two arene molecules at axial positions. The η^6-coordination of an arene molecule to only one bismuth atom in **3** is slightly tighter, but otherwise very similar to that in **2** with the 3.10 Å Bi-to-ring center distance and 15.8° deviation from perpendicularity. The length of the Bi−Bi bond and other dimensions of the dimetal unit in the adducts **2** and **3** vary slightly compared to the characteristics of pure bismuth(II) trifluoroacetate (**1**). That implies that interaction of the bismuth atom with the aromatic system in arenes is relatively weak and does not disturb the dimetal unit. It is worth noting that hexamethylbenzene tremendously enhances the stability of **1**, so that the crystals of the adduct are stable in open air for days. At the same time, the crystals of adducts with toluene (**2**) and *p*-xylene (**3**) are still vulnerable when exposed to open atmosphere, but to a lesser degree than pure trifluoroacetate.

Conclusions. New bismuth(II) trifluoroacetate is the first "inorganic" salt of bismuth in oxidation state +2 that has been obtained in pure form with quantitative yield. The fact that this compound remains intact in aromatic solvents and in the vapor phase makes it attractive to study its chemistry

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using both solution and solid state approaches. Our preliminary results indicate an intriguing reactivity of **1** toward various transition metal complexes and electron-deficient molecules, as well as some organic substrates. We shall report these new findings shortly.

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Supporting Information Available: Four X-ray crystallographic files, in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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