Ab Initio Structure Determination from X-ray Powder Diffraction Data of Tetraaquabismuth(III) Triflate Obtained from the Nonahydrate

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The thermal decomposition of nonaaquabismuth(III) triflate has been studied by thermogravimetric analysis, from which lower hydrates have been identified. The crystal structure of the tetraaquabismuth(III) triflate, $Bi(H_2O)_4(OSO_2CF_3)_3$, has been solved ab initio from powder data collected with conventional monochromatic X-rays even though the asymmetric unit cell contains 29 atoms and 93 atomic coordinates to refine. The structure is built from discrete dimers in which the Bi atoms are 8-fold coordinated to four water molecules and four oxygen atoms belonging to three triflate groups. The structure differences with respect to that of the precursor are discussed.

Introduction

Several accounts of various applications of rare-earth chemistry in organic synthesis have been reported during the past decade.[1] Among them, a marked interest in the activity of rare earths as Lewis acid catalysts can be noted, particularly for the trifluoromethanesulfonates (triflates).[2]

The applications in organic synthesis of bismuth(V) compounds[3] and the use of Bi(III) oxide in the oxidation of alkenes (SOHIO process)[4] are well-known. More recently, the catalytic properties of Bi(III) compounds have been reported for Mukaiyama aldol[5] and Michael[5a−c] reactions, halosilane activation,[6] carbonylene[7] and Diels−Alder[8] reactions, acylations,[9] especially Friedel−Crafts acylations,[9d,e] and other reactions such as the oxidation of α-ketols[10] or epoxides[11] and for the Knoevenagel condensation.[12]

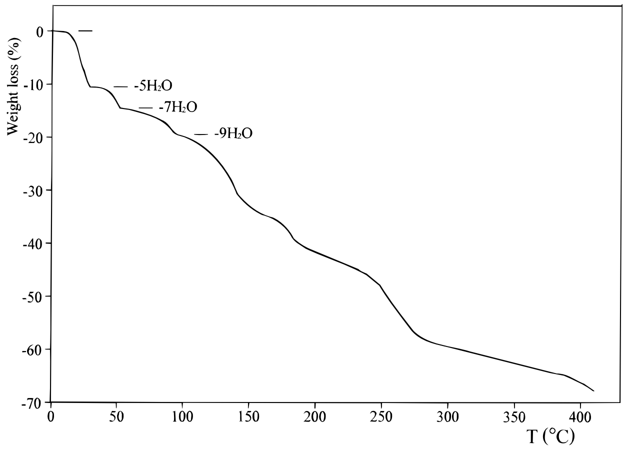

Figure 1. TG curve in flowing nitrogen of $Bi(H_2O)_9(OSO_2CF_3)_3$ (heating rate 5 °C h^{-1}).

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Table 1. Crystallographic Data and Details of the Rietveld Refinement for $Bi(H_2O)_4(OSO_2CF_3)_3$

formula wt (g)	728.08
crystal system and space group	monoclinic $P2_1/c$
a (Å)	18.977(2)
b (Å)	8.0034(9)
c (Å)	21.918(3)
β (deg)	146.503(6)
V (Å^3)	1386
M_{20}	41
F_{30}	99(0.0076, 40)
Z	4
wavelength (Å)	1.540598
step increment (deg 2θ)	0.02
2θ range (deg)	14−90
no. of reflections	1572
no. of structural parameters	93
no. of profile parameters	16
no. of non-hydrogen atoms	29
R_F	0.04
R_B	0.07
R_P	0.08
R_{wP}	0.11

Table 2. $Bi(H_2O)_4(OSO_2CF_3)_3$: Positional and Thermal Parameters with Standard Deviations

atom	x	y	z	B_{iso} (Å^2)[a]
Bi	0.6470(3)	0.1061(3)	0.5158(3)	1.5(1)
S1	0.394(1)	0.758(2)	0.363(1)	2.1(3)
S2	0.852(2)	0.751(2)	0.731(2)	2.1(3)
S3	0.668(2)	0.744(2)	0.413(1)	2.1(3)
O11	0.307(3)	0.761(4)	0.348(3)	2.4(4)
O12	0.448(3)	0.915(3)	0.392(3)	2.4(4)
O13	0.460(3)	0.612(3)	0.407(2)	2.4(4)
C1	0.277(3)	0.747(4)	0.212(3)	4.0(9)
F11	0.221(3)	0.604(3)	0.179(3)	6.9(4)
F12	0.333(3)	0.741(4)	0.200(3)	6.9(4)
F13	0.203(3)	0.871(3)	0.162(3)	6.9(4)
O21	0.823(3)	0.584(3)	0.695(3)	2.4(4)
O22	0.944(3)	0.821(3)	0.753(3)	2.4(4)
O23	0.749(3)	0.858(3)	0.668(3)	2.4(4)
C2	0.936(3)	0.761(4)	0.868(3)	4.0(9)
F21	0.862(3)	0.702(3)	0.856(3)	6.9(4)
F22	1.039(3)	0.664(3)	0.935(3)	6.9(4)
F23	0.967(3)	0.914(3)	0.900(3)	6.9(4)
O31	0.620(3)	0.575(3)	0.386(3)	2.4(4)
O32	0.598(3)	0.850(3)	0.323(2)	2.4(4)
O33	0.688(3)	0.828(3)	0.485(2)	2.4(4)
C3	0.837(3)	0.735(4)	0.503(2)	4.0(9)
F31	0.812(3)	0.652(3)	0.437(2)	6.9(4)
F32	0.907(3)	0.639(4)	0.590(2)	6.9(4)
F33	0.883(3)	0.886(3)	0.530(2)	6.4(4)
Ow1	0.699(3)	0.388(4)	0.540(3)	1.4(5)
Ow2	0.437(3)	0.263(4)	0.385(3)	1.4(5)
Ow3	0.563(3)	0.165(4)	0.353(3)	1.4(5)
Ow4	0.888(3)	0.118(4)	0.662(3)	1.4(5)

[a] Atoms of the same kind have been constrained to have the same isotropic *B* factors.

Table 3. $Bi(H_2O)_4(OSO_2CF_3)_3$: Selected Bond Distances (Å) and Angles (deg)[a]

		Bi Polyhedron		
Bi	Ow1	2.34(4)		
	Ow3	2.44(5)		
	O11^{I}	2.54(5)		
	Ow2	2.57(6)		
	Ow4	2.60(6)		
	O12^{II}	2.62(5)		
	O33^{II}	2.63(4)		
	O23^{II}	2.84(3)		
		Triflate Groups		
S1	O11	1.39(8)	O11−S1−O12	112(7)
	O12	1.40(4)	O11−S1−O13	113(7)
	O13	1.36(4)	O11−S1−C1	99(6)
	C1	1.91(4)	O12−S1−O13	124(3)
			O12−S1−C1	100(3)
			O13−S1−C1	104(3)
C1	F11	1.30(5)	S1−C1−F11	104(3)
	F12	1.28(9)	S1−C1−F12	113(7)
	F13	1.26(6)	S1−C1−F13	108(4)
			F11−C1−F12	106(9)
			F11−C1−F13	114(4)
			F12−C1−F13	112(9)
S2	O21	1.41(3)	O21−S2−O22	111(5)
	O22	1.47(8)	O21−S2−O23	117(4)
	O23	1.40(5)	O21−S2−C2	110(4)
	C2	1.89(5)	O22−S2−O23	113(7)
			O22−S2−C2	105(6)
			O23−S2−C2	100(4)
C2	F21	1.30(9)	S2−C2−F21	109(6)
	F22	1.34(6)	S2−C2−F22	104(4)
	F23	1.30(4)	S2−C2−*F*23	108(4)
			F21−C2−F22	111(8)
			F21−C2−*F*23	112(7)
			F22−C2−*F*23	112(5)
S3	O31	1.45(4)	O31−S3−O32	117(4)
	O32	1.41(3)	O31−S3−O33	112(4)
	O33	1.45(6)	O31−S3−C3	109(5)
	C3	1.91(7)	O32−S3−O33	110(5)
			O32−S3−C3	106(4)
			O33−S3−C3	102(6))
C3	F31	1.27(7)	S3−C3−F31	98(6)
	F32	1.34(4)	S3−C3−F32	108(4)
	F33	1.31(5)	S3−C3−F33	110(5)
			F31−C3−F32	109(5)
			F31−C3−F33	119(5)
			F32−C3−F33	113(4)
		Possible Hydrogen Bonds		
Ow1	O21	2.49(5)	O21−Ow1−O31	105(3)
	O31	2.73(6)		
Ow2	O13	2.80(4)	O13−Ow2−O23^{I}	112(3)
	O23^{I}	2.81(9)		
Ow3	O32^{III}	2.60(4)		
Ow4	O22^{IV}	2.52(7)		

[a] Symmetry code: I: $1 - X, 1 - Y, 1 - Z$; II: $X, Y - 1, Z$; III: $1 - X, Y - 0.5, 0.5 - Z$; IV: $-X + 2, Y - 0.5, 1.5 - Z$.

While most of this work involves the catalytic properties of halides BiX_3,[5−9,12] we have recently observed an outstanding activity of triflate $Bi(OSO_2CF_3)$ (**1**) in the Mukaiyama aldol[5e] and Diels−Alder[8] reactions. In 1995, Frank and co-workers[13] have isolated from a saturated solution of **1** in aqueous triflic acid a crystalline form of $Bi(H_2O)_9(OSO_2CF_3)_3$, isotypic to nonaaqualanthanoid(III) triflates.[14] Previously, **1** has been described as a hygroscopic solid.[15]

Before extending the synthetic applications of **1**, it appeared to us necessary to study its thermal stability and its hydration degree as a function of temperature. Moreover, the only anhydrous metallic triflate to have been structurally characterized is $LiOSO_2CF_3$,[16] and the structure of a heavy metallic triflate other than in the nonahydrated cation state is still unknown.[14] This situation can be explained by the difficulty in obtaining single crystals of lower hydrates, usually obtained in a powder form from thermal decomposition. Nevertheless, with the spectacular progress in powder diffrac-

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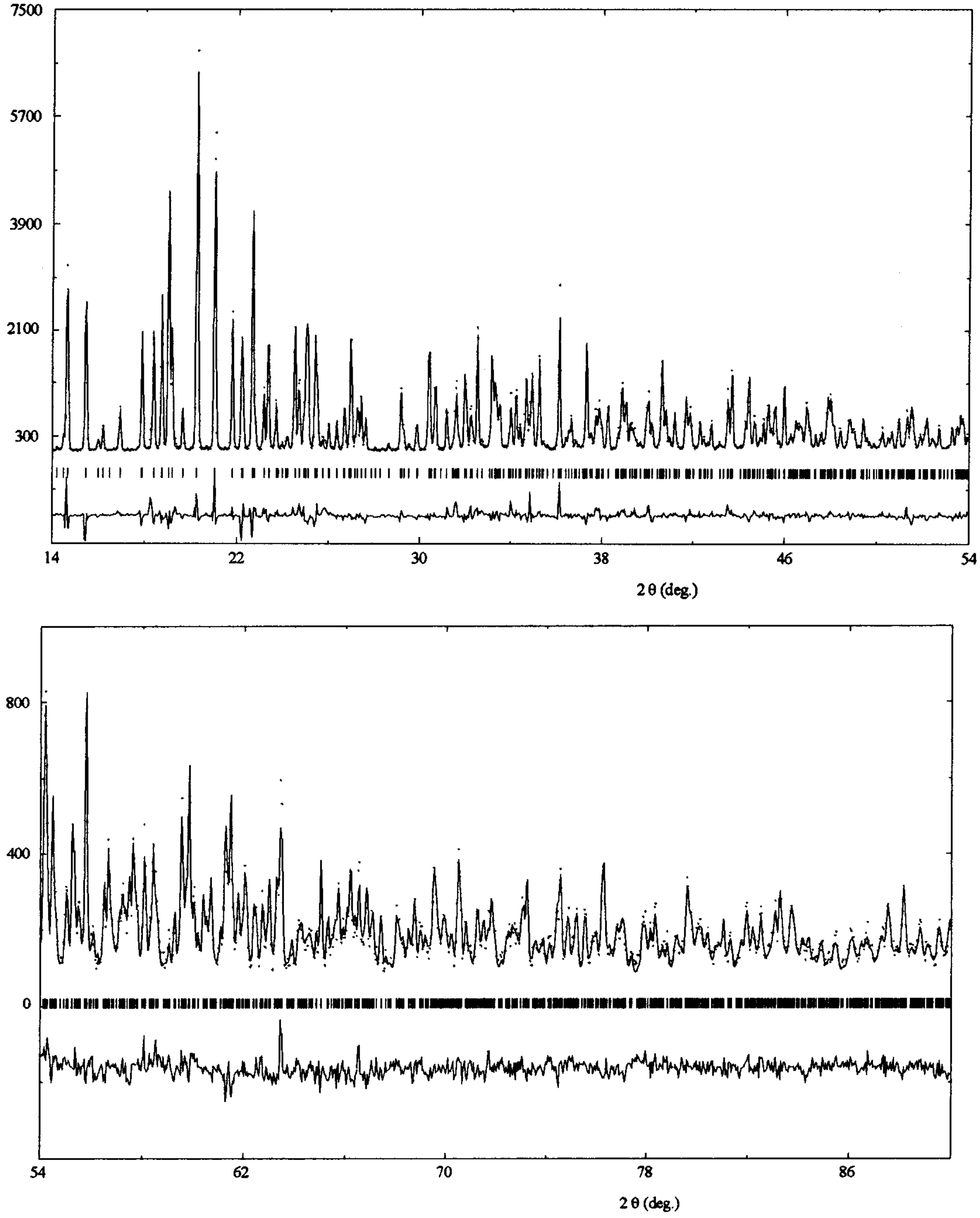

Figure 2. Final Rietveld plot for $Bi(H_2O)_4(OSO_2CF_3)_3$. The upper trace shows the observed data as dots, while the calculated pattern is shown by the solid line. The lower trace is a plot of the difference: observed minus calculated. Note that the intensity scale is different for the high-angle region.

tion[17] that has occurred in the past few years, there is now an opportunity to investigate moderately complex crystal structures from powder diffraction data. This last application of modern powder crystallography has been reviewed recently.[18] Powder diffraction patterns of solids obtained from thermal decomposition are often degraded by diffraction line broadening arising from the microstructure. Therefore, these powder solids constitute the *real world* of powders since single crystals cannot be obtained by this preparation route. There is obviously a great interest in the knowledge of the structure of these decomposition products to explain the mechanism of solid-state thermal transformations. The present study deals with the crystal structure of tetraaquabismuth(III) triflate ($Bi(H_2O)_4(OSO_2CF_3)_3$), determined ab initio from X-ray diffraction powder data and with its synthesis from the thermal decomposition of the nonahydrate.

Experimental Section

Preparation of Bismuth(III) Trifluoromethanesulfonate (1). Bismuth triflate was prepared from procedures described elsewhere from triflic acid and bismuth(III) acetate.[15a] The white powder obtained was washed with dichloromethane and heated at 60 °C under reduced pressure (0.1 mmHg) until a constant weight was reached. Elemental analysis was in agreement with a mixture of hydrated forms of **1**. Anal. Calcd for $C_3H_4BiF_9O_{11}S_3$ (**1**$\cdot 2H_2O$): C, 5.20; H, 0,58; Bi, 30.19; F, 24.70; S, 13.90. Anal. Calcd for $C_3H_8BiF_9O_{13}S_3$ (**1**$\cdot 4H_2O$): C, 4.95; H, 1.10; Bi, 28.69; F, 23.48; S, 13.21. Found: C, 5.1; H, 0.7; Bi, 29.0; F, 23.9; S, 13.5. ^{13}C NMR (CD_3COCD_3) 120 ppm (from TMS), quartet, $^1J(^{13}C/^{19}F) = 321$ Hz; ^{19}F NMR (CD_3-

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$COCD_3$) 0.84 ppm (from CF_3COOH). IR (Nujol) 3450−3550 (mb), 1230−1290 (vs), 1180 (s), 1034 (s), 1028 (sh), 650 (sh), 643 (s).

When the sample is heated between 70 and 90 °C under reduced pressure, a weight loss and a darkening of the powder are observed, due to a slow decomposition that makes difficult the preparation of pure anhydrous **1**. On the other hand, in air and at room temperature this sample transforms into a pure nonahydrate phase $Bi(H_2O)_9(OSO_2CF_3)_3$. The last was identified from its powder diffraction data and pattern indexing, giving unit-cell dimensions in agreement with the results reported by Frank et al.[13] This precursor was used to synthesize the tetrahydrate, by heating it at 50 °C. The tetrahydrate is stable at room temperature in a nitrogen atmosphere.

Thermogravimetry. Thermogravimetric analysis was carried out with a Thermoflex Rigaku TG-DSC instrument. The decomposition was performed in a nitrogen atmosphere until 400 °C with a heating rate of 5 °C h^{-1}.

X-ray Powder Diffraction. Precise X-ray powder diffraction data were collected at room temperature with a high-resolution diffractometer (Siemens D500), equipped with an incident-beam monochromator to select monochromatic copper $K\alpha_1$ radiation.[19] The pattern was scanned in the range 8−90° (2θ) with a step length of 0.02° (2θ) and a counting time of 50 s $step^{-1}$. To prevent hydration, the sample was kept in a nitrogen atmosphere by using an airtight sample holder. For pattern indexing the Bragg peak positions were extracted by the pattern decomposition technique with the fitting program PROFILE from Socabim, available in the software package DIFFRACT-AT supplied by Siemens. Pattern indexing was carried out by the successive dichotomy method[20] by means of the program DICVOL91.[21] The programs EXTRA[22] and SIRPOW.92[23] were used to solve the structure and FULLPROF[24] for its refinement by the Rietveld method.

Results

The TG curve of the thermal decomposition of the precursor is shown in Figure 1. The complete mechanism of the decomposition is complex. However, the first plateau in the temperature range 39−52 °C is well defined. It corresponds to the loss of 5 water molecules (theoretical weight loss 11%) and, consequently, to the formation of the tetrahydrate phase, $Bi(H_2O)_4(OSO_2CF_3)_3$. Two other stages, poorly defined (weight losses 15.4 and 19.8%, in the approximate temperature ranges 54−62 and 93−100 °C) should correspond to the loss of seven and nine water molecules respectively, i.e., to the formation of $Bi(H_2O)_2(OSO_2CF_3)_3$ and $Bi(OSO_2CF_3)_3$. The decomposition of anhydrous **1** would begin around 100 °C, in accordance with our attempts to isolate anhydrous **1** (see Experimental Section). The final product of the decomposition, identified from powder diffraction, corresponds to BiF_3 (theoretical weight loss 67.5%).

Indexing. The indexing of the powder pattern of the tetrahydrate phase gave a unique monoclinic solution with satisfactory figures of merit [$M_{20} = 36$, $F_{20} = 96(0.0057,37)$]. The complete powder diffraction data were reviewed by means of a least-squares procedure giving the final cell dimensions listed in Table 1. The powder data have been submitted to the ICDD[25] for possible inclusion in the Powder Diffraction File. The systematic absences suggested space group $P2_1/c$. From this unit cell, no chemically related isostructural material was found by searching the NIST-CDF database.[25]

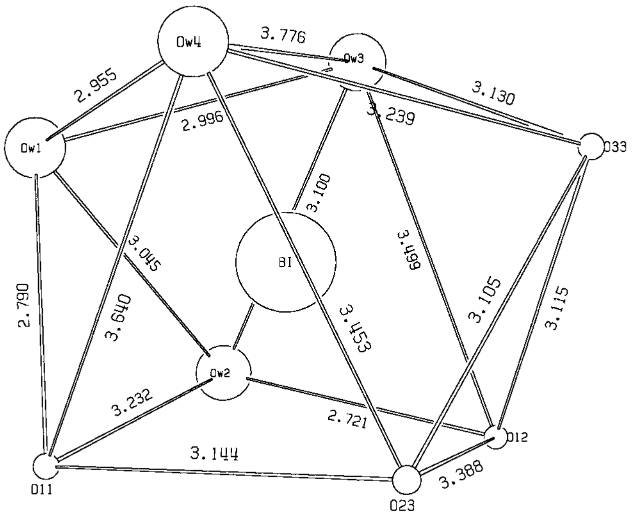

Figure 3. ORTEP plot of the polyhedron around Bi.

Structure Solution and Refinement. Integrated intensities were extracted by means of the program EXTRA from which 1572 structure-factor amplitudes were obtained, including 28% symmetry-independent reflections, in the range 14−90° (2θ) since diffraction information was not reliable at higher angles. They were input in the direct-methods program SIRPOW.92. The top four peaks were assigned to one Bi and three S atoms. Additionally, from geometric considerations, nine O atoms and three F atoms were easily recognized. The rest of the structure was found from several subsequent difference Fourier calculations. This approximate solution was used as the starting structural model for a Rietveld refinement. A pseudo-Voigt function was selected to describe individual line profiles, and the usual quadratic function in tan θ was used to describe the angular dependence of peak widths. Five coefficients were used to describe the functional dependence of the background. The conditions of the refinement are listed in Table 1. Figure 2 shows the final fit obtained between calculated and observed patterns. Atomic coordinates are given in Table 2, and selected bond distances and angles in Table 3.

Description of the Structure. The Bi atom is 8-fold coordinated to four water molecules and four oxygen atoms belonging to three triflate groups. The Bi−Ow distances range from 2.34(4) to 2.60(6) Å and agree well with those found in the structure of the precursor $Bi(H_2O)_9(OSO_2CF_3)_3$[13] (2.45−2.58 Å), in which the Bi atoms are 9-fold coordinated in the form of isolated $Bi(H_2O)_9^{3+}$ cations and the triflate groups are connected only by hydrogen bonds. In the tetrahydrate, the triflate groups are coordinated to Bi atoms. This is a consequence of the departure of five water molecules from the structure of the precursor. The Bi−O(triflate) distances range from 2.57(6) to 2.81(4) Å. To our knowledge there is no compound with Bi bonded to triflate groups reported in the literature. However, the bond lengths can be compared to those found, for

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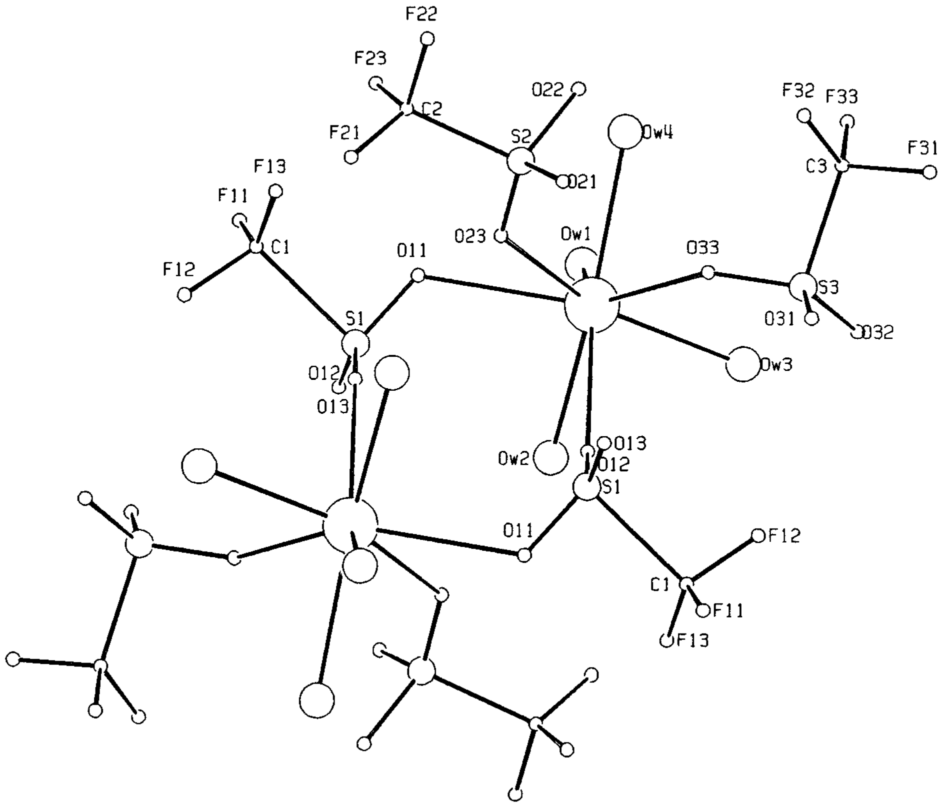

Figure 4. ORTEP plot of a dimer.

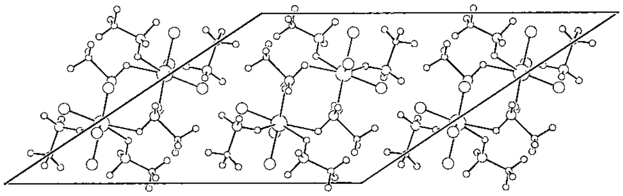

Figure 5. Projection of the structure along [010].

instance, in $Bi_2(OCOCH_3)_6·3SC(NH_2)·2H_2O$,[26] i.e., 2.34–2.78 Å. The polyhedron around Bi can be described as a distorted bicapped trigonal prism shown in Figure 3. Among the three independent triflate groups, two are bonded by only one O atom (S2 and S3) and the other (S1) bridges two Bi atoms (Bi–O11 and Bi–O12) in order to form the dimer shown in Figure 4. There are two such isolated dimers in the unit cell (Figure 5). They are linked together by hydrogen bonds only (see Table 3).

The accuracy on the atomic positions of the lighter atoms is not high, as shown by the spread of S–O, S–C, and C–F distances in the triflate groups. This is the consequence of various factors: the high scattering contrast between the heavy atom and the other atoms, the limited resolution of the X-ray diffraction data for a decomposition product and, additionally, the great number of variable parameters for a powder diffraction study. However, the solution is precise enough for the description of the structure. Indeed, the geometry of the triflate group is reasonably defined within 2 esd's. For comparison, it can be noted that in a study of the anhydrous compound $LiOSO_2CF_3$,[16] for which the contrast between scatterers is considerably more favorable, the spread in the distances was lower, as expected.

Conclusion

From TG analysis of the decomposition of $Bi(H_2O)_9(OSO_2CF_3)_3$ it has been shown that the dehydration begins at relatively low temperature (40 °C), giving a tetrahydrate that can be stabilized at room temperature in a nitrogen atmosphere. A dihydrate appears above 60 °C, and the anhydrous compound is formed at about 100 °C. These temperatures are lower than those reported for the decomposition of lanthanum triflate,[27] which is an indication of a greater lability of the water molecules in the hydrated forms of **1**. Despite a powder diffraction pattern with limited accuracy the crystal structure of $Bi(H_2O)_4(OSO_2CF_3)_3$ has been completely solved ab initio from conventional X-ray diffraction powder data. The complexity of the structure (29 atoms in the asymmetric unit cell and 92 structural parameters) for a powder diffraction study should be noted. Indeed, it can be compared to noteworthy complex examples reported in the recent years.[28,30] Finally, by comparison with the structure of the precursor $Bi(H_2O)_9(OSO_2CF_3)_3$, built from isolated $Bi(H_2O)_9^{3+}$ cations, it is shown that the triflate groups are bonded to the Bi atom in the tetrahydrate, resulting in a condensation of Bi atoms into dimers. Clearly, the determination of the structure of the lower hydrate and the anhydrous phase would be of interest for a complete understanding of the crystal chemistry of this family of compounds.

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