SYNTHESIS AND CRYSTAL STRUCTURE OF BISMUTH(III) TRIFLUOROACETATE-TRIFLUOROACETIC ACID ADDUCT, $Bi(OOCCF_3)_3.HOOCCF_3$

Guido J. Reiß, Walter Frank* and Jürgen Schneider

Fachbereich Chemie, Universität Kaiserslautern
Erwin Schrödinger Straße, D-67663 Kaiserslautern, Germany

Abstract: The 1:1 adduct of bismuth(III) trifluoroacetate with trifluoracetic acid **1** was prepared from bismuth(III) oxide, trifluoroacetic anhydride and trifluoroacetic acid in dichloromethane. Crystals were grown from trifluoroacetic acid and the crystal structure could be determined by X-ray diffraction methods. **1** crystallizes in the centrosymmetric space group $P2_1/n$ with a = 9.096(2) Å, b = 8.535(2) Å, c = 22.205(4) Å, β = 95.25(3)°, Z = 4; R = 8.71 %, R_W = 7.81 for all data with $I > 0$. The bismuth atom has a highly asymmetric coordination polyhedron with nine relevant Bi - O distances in the range of 2.26(3) to 2.90(3) Å. Three short Bi - O distances between 2.26(3) and 2.27(3) Å and corresponding O - Bi - O angles from 80.0 to 81.0° reflect the lonepair situation of bismuth in this compound. The structure is built up by infinite chains along the crystallographic b axis. Three trifluoroacetate groups and the trifluoroacetic acid molecule are bound to the bismuth atoms via their C - O functions. Two of the trifluoroacetate groups act as 'tridentate' bridging ligands between a bismuth atom and its two symmetry dependant neighbours in the chain. The third trifluoroacetate group and the trifluoroacetic acid molecule are connected by a strong O-H...O hydrogen bridge. Both parts form an unidentate coordination to a bismuth atom and together they act as a new bidentate bridging ligand on both sides between every second part of the chain.

Introduction

In the course of our investigations on the structural chemistry of bismuth(III) complexes we had to synthesize bismuth(III) trifluoroacetate as starting material. Its preparation was described earlier by three authors who reported very different synthetic pathways [1]. Following the procedures described by Fujioka and Cady [1] we did not obtain the bismuth(III) trifluoroacetate but rather the bismuth(III) trifluoroacetate-trifluoracetic acid adduct **1**.

Only a few structurally characterized acetates [2] and trifluoroacetates [3] of trivalent main group metals have been reported. Adducts of metal acetate and acetic acid or its organo-substituted derivatives are very common [4], but no such compound of a trivalent main group metal has been structurally characterized. In the following sections we will report the synthesis of the bismuth(III) trifluoroacetate-trifluoroacetic acid adduct **1** and give a description of its crystal structure.

Results and Discussion

The new compound **1** is the main product from the synthesis of bismuth(III) trifluoroacetate if an excess of trifluoroacetic acid is present. Removal of the trifluoroacetic acid molecule can be done by slowly heating the crystalline material in vacuo. This procedure yielded a white powder of pure bismuth(III) trifluoroacete.

In the crystal structure of **1** the bismuth atom is surrounded by nine oxygen atoms that form a highly asymmetric coordination polyhedron (Fig. 1). There are three short Bi - O distances in of about 2.27(3) Å and corresponding O - Bi - O angles from 80.0 to 81.0° and six additional Bi - O distances that vary between 2.64(3) and 2.90(3) Å. A great variety of Bi - O bond lengths is a common feature in related bismuth compounds [5]. Remarkably the three longest Bi - O distances are those that are *trans* to the three shortest Bi - O bonds. The coordination polyhedron with three very short Bi - O bonds nearly perpendicular to each other is reminiscent of the lighter group 15 homologues. The structure is built up from polymeric chains along the crystallographic b axis. A classification and a detailed description of the different coordination modes of acetate groups at metal atoms is given by Ouchi et al. [6].

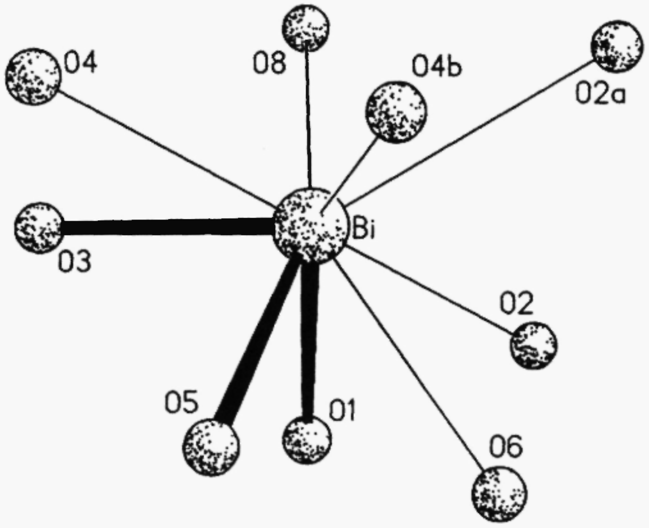

Fig. 1 Coordination polyhedron of the bismuth atom in **1**

Three trifluoroacetate groups and the trifluoroacetic acid molecule are bound to the bismuth atoms via their C - O functions. Two of the trifluoroacetate groups act as 'tridentate' bridging ligands between a bismuth atom and its two symmetry dependent neighbours in the chain. The third trifluoroacetate group and the trifluoroacetic acid molecule are connected by a strong O-H...O hydrogen bond. The bond order of this hydrogen bond is empirically calculated to be 0.20 (Table 1). Both parts form an unidentate coordination to a bismuth atom and together they act as a new bidentate bridging ligand on both sides between every second chain link. They are nearly perpendicular to the chain-propagating tridentate bridges (Fig. 2). The geometry of this two-stage bridge ligand probably causes the Bi - Bi distances of two additionally bridged bismuth atoms [Bi - Bi(a)] in the chain to be 0.33 Å longer than the distance of the exclusively 'tridentate'-acetate-bridged bismuth atoms [Bi - Bi(b) and Bi(a) - Bi(c)] (Fig. 2).

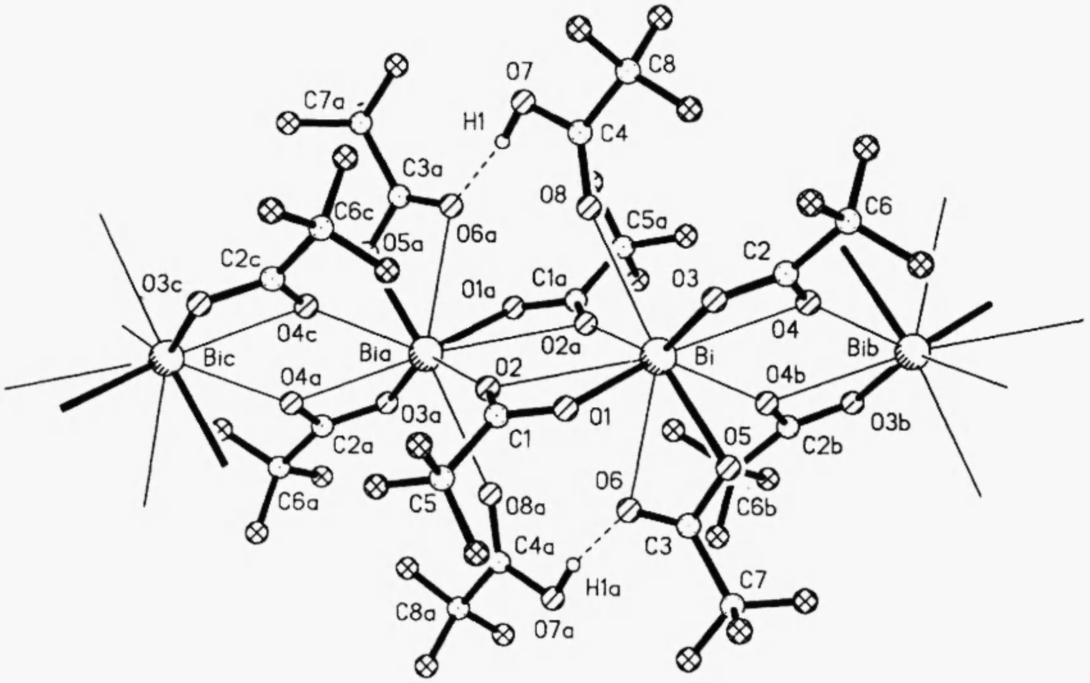

Fig. 2 Part of the chain in **1** along [0 1 0]
symmetry code a = -x, 1-y, -z; b = -x, -y, -z; c = x, 1+y, z

Table 1. Selected geometric parameters (Å, °)
values in square brackets are calculated bond orders

Bi-O(1)	2.26 (3)	[0.65]	Bi-O(3)	2.27 (3)	[0.62]
Bi-O(5)	2.26 (3)	[0.65]	Bi-O(4)	2.64 (3)	[0.23]
Bi-O(6)	2.65 (3)	[0.23]	Bi-O(8)	2.71 (3)	[0.19]
Bi-O(2)	2.91 (3)	[0.11]	Bi-O(2a)	2.84 (3)	[0.14]
Bi-O(4b)	2.79 (3)	[0.15]	O(6a)-O(7)	2.70 (4)	[0.20]
H(1)-O(7)	0.84		H(1) ... O(6a)	1.84	
Bi-Bi(a)	4.900 (3)		Bi ... Bi(b)	4.561 (3)	
O(1)-C(1)	1.29 (4)		O(2)-C(1)	1.22 (4)	
O(3)-C(2)	1.27 (4)		O(4)-C(2)	1.24 (4)	
O(5)-C(3)	1.27 (4)		O(6)-C(3)	1.25 (3)	
O(7)-C(4)	1.33 (4)		O(8)-C(4)	1.23 (4)	
C(1)-C(5)	1.49 (4)		C(2)-C(6)	1.51 (4)	
C(3)-C(7)	1.49 (3)		C(4)-C(8)	1.51 (4)	

all C-F distances are set to 1.325 Å; symmetry code a = -x, 1-y, -z; b = -x, -y, -z.

O(1)-Bi-O(3)	81.2(11)	O(1)-Bi-O(4)	127.7(9)
O(3)-Bi-O(4)	50.4(9)	O(1)-Bi-O(5)	79.6(10)
O(3)-Bi-O(5)	80.6(10)	O(4)-Bi-O(5)	74.5(9)
O(1)-Bi-O(6)	69.8(10)	O(3)-Bi-O(6)	127.4(9)
O(4)-Bi-O(6)	121.2(8)	O(5)-Bi-O(6)	52.3(8)
O(1)-Bi-O(8)	92.7(11)	O(3)-Bi-O(8)	78.8(10)
O(4)-Bi-O(8)	95.6(10)	O(5)-Bi-O(8)	158.9(10)
O(6)-Bi-O(8)	142.8(9)	Bi-O(8)-C(4)	159.8(17)
O(1)-C(1)-O(2)	122.0(29)	O(1)-C(1)-C(5)	110.3(25)
O(2)-C(1)-C(5)	126.1(27)	O(3)-C(2)-O(4)	115.1(34)
O(3)-C(2)-C(6)	124.0(27)	O(4)-C(2)-C(6)	120.3(26)
O(5)-C(3)-O(6)	120.4(27)	O(5)-C(3)-C(7)	112.1(24)
O(6)-C(3)-C(7)	126.4(27)	O(7)-C(4)-O(8)	115.0(33)
O(7)-C(4)-C(8)	117.0(28)	O(8)-C(4)-C(8)	128.0(31)
O(6a)-H(1)-O(7)	168(4)		

Experimental

Starting materials: bismuth(III) oxide, trifluoroacetic anhydride and trifluoroacetic acid were commercially available und purified by standard methods [7].

Synthesis: 5.5 g (11.5 mmol) bismuth(III) oxide are suspended in a mixture of 5.1 ml (35.4 mmol) trifluoroacetic anhydride and 15 ml dichloromethane under an atmosphere of dried argon. 10 ml (139 mmol) trifluoroacetic acid was slowly added at room temperature. The mixture was stirred for an additional hour. Colourless twinned needles formed after 24 hours at 0°C. Yield 94 %. Recrystallization from trifluoroacetic acid over several weeks at 0°C yielded small colourless single crystals of **1**.

Crystallographic study

Setting: A suitable single crystal (0.2 x 0.1 x 0.1 mm^3), was sealed in a capillary and mounted on a Siemens P4 diffractometer operating with graphite-monochromated MoKα X-radiation. The cell constants were refined by least-squares methods using 20 centered reflections in the range $20 > 2\Theta > 22°$

Data Collection: Intensity data were collected by ω-scans in the range $-8 > h > 8$, $0 > k > 8$, $0 > l > 21$ ($2\Theta_{max.}$ = 40.1°). Remeasurement of three standard reflections indicated no decay over the time of exposure at room temperature. 1715 reflections were measured yielding 1610 observed reflections with $I > 0$, of which 1179 reflections were unique (R_{int} = 0.033).

Crystal data: C_8 H O_8 F_{12} Bi, monoclinic, space group $P2_1/n$ (No. 14), a = 9.096(2) Å, b = 8.535(2) Å, c = 22.205(4) Å, β = 95.25(3)°, V = 1716.6(6) $Å^3$, Z = 4, μ = 104.3 cm^{-1}, F(000) = 1216.

Solution and refinement: All calculations were carried out with the software package SHELXTL plus [8]. Due to the weakly diffracting crystal only poor data were collected. The structure was solved by Patterson methods locating the bismuth atom. Repeated ΔF synthesis yielded all C, O and F atom positions. In the early stages of refinement rigid models of trifluoroacetate groups were used. Convergence was achieved in an isotropic refinement with restrained C - F distances set to 1.325 Å (C - F distance according to the literature [9]) and damping. To get a tolerable reflection to parameter ratio in the final stages of refinement only the bismuth and the fluorine atoms were refined with anisotropic displacement parameters. Data were weighted according to $w^{-1} = \sigma^2(F)$ and an extinction parameter was refined to $\chi = 0.00071(9)$ where $F^* = F[1+0.002\,\chi\,F^2/\sin 2\Theta]^{-1/4}$. The refinement converged to a R_W-value of 7.81 % (R = 8.71 %) for all data with $I > 0$ ($\Delta\rho_{max.}$ = 2.30 e$Å^{-3}$ near bismuth).

Table 2. Fractional atomic coordinates and equivalent isotropic displacement parameters ($Å^2$)

	x/a	y/b	z/c	U(eq)[8]
Bi	0.1125(2)	0.2390(2)	0.0026(1)	0.033(1)
O(1)	0.304(3)	0.385(3)	0.0421(16)	0.059(8)
O(2)	0.141(3)	0.573(3)	0.0264(14)	0.055(8)
O(3)	0.299(3)	0.104(3)	-0.0351(14)	0.051(8)
O(4)	0.118(3)	-0.053(3)	-0.0362(14)	0.039(7)
O(5)	0.189(3)	0.094(3)	0.0847(13)	0.032(7)
O(6)	0.082(3)	0.304(2)	0.1174(13)	0.040(7)
O(7)	0.068(3)	0.511(3)	-0.1884(15)	0.073(9)
O(8)	0.116(3)	0.372(4)	-0.1079(14)	0.078(9)
C(1)	0.262(3)	0.529(3)	0.0470(15)	0.024(9)
C(2)	0.240(3)	-0.024(3)	-0.054(2)	0.040(9)
C(3)	0.148(4)	0.177(3)	0.1279(11)	0.023(9)
C(4)	0.132(4)	0.385(4)	-0.1620(14)	0.044(10)

C(5)	0.364(2)	0.613(3)	0.0922(13)	0.068(11)
F(1)	0.3101	0.7558	0.0989	0.164(8)
F(2)	0.4921	0.6234	0.0684	0.165(8)
F(3)	0.3839	0.5436	0.1456	0.193(8)
C(6)	0.319(2)	-0.146(2)	-0.0888(13)	0.056(10)
F(4)	0.4514	-0.0904	-0.0971	0.136(7)
F(5)	0.2449	-0.1735	-0.1420	0.160(8)
F(6)	0.3323	-0.2775	-0.0573	0.161(8)
C(7)	0.164(3)	0.091(3)	0.1867(9)	0.68(11)
F(7)	0.1151	0.1841	0.2283	0.173(8)
F(8)	0.3055	0.0603	0.2009	0.143(8)
F(9)	0.0877	-0.0415	0.1842	0.174(8)
C(8)	0.212(3)	0.277(3)	-0.2016(12)	0.090(11)
F(10)	0.2649	0.1530	-0.1707	0.157(8)
F(11)	0.3213	0.3496	-0.2257	0.130(7)
F(12)	0.1123	0.2306	-0.2453	0.158(8)
H(1)	0.0259	0.5629	-0.1612	0.050

Bond order calculations

Based on the concept introduced by L. Pauling [10] and refined by I.D. Brown et al. [11], bond order for Bi - O interactions have been calculated, the B parameter being set at 0.37 and r_0 = 2.094 was taken as standard bond length. The sum of bond valences at the bismuth atom has been calculated as 2.95 (Table 1)

References

[1] a) C.D. Garner and B. Hughes, *Inorg. Chem.* **1975,** *14*, 1722; b) P.V. Radheshwar, R. Dev and G.H. Cady, *J. Inorg. Nucl. Chem.* **1972,** *34*, 3914; c) G.S. Fujioka and G.H. Cady, *J. Am. Chem. Soc.* **1957**, *79*, 2451.

[2] a) F.A. Cotton and W.H. Isley, *Inorg. Chem* **1982**, *21*, 300; b)M.Hall and D.B. Sowerby, *J.Chem. Soc. Dalton Trans.* **1980**,1292; c) I.D. Brown and R. Faggiani, *Acta Crystallogr.* **1978,** *B34*, 2845; d) I.D. Brown and R. Faggiani, *Acta Crystallogr.* **1982,** *B38*, 2473.

[3] a) D.P. Bullivant, M.F.A. Dove and M.J. Haley, *J.Chem.Soc. Dalton Trans.* **1980**, 105; b) S.R. Breese, L. Chen and S. Wang, *J. Chem. Soc. Dalton Trans.* **1994**, *2545*.

[4] a) A. Lossin, G. Meyer, F. Fuchs and J. Strähle, *Z. Naturforsch.* **1992**, *B47*, 179; b) T.C.W Mak, W.-H. Yip, W.-H. Chan, C.H.L. Kennard, G. Smith and E. O'Reilly, *Polyhedron*, **1989**, *8*, 793; c) T.C.W Mak, W.-H. Yip, G. Smith and E. O'Reilly and C.H.L. Kennard, *Inorg. Chim. Acta,* **1984,** *88*, 35; d) T.C.W Mak, W.-H. Yip, C.H.L. Kennard and G. Smith, *Aust. J. Chem.*, **1990**, *43*, 1431.

[5] a) B. Romero, S. Bruque, M.A.G. Aranda and J.E. Iglesias, *Inorg Chem.* **1994,** *33,* 1869; b) F. Lazarini, *Acta Crystallogr.* **1979,** *B35*, 448; c) F. Lazarini, *Cryst. Struct. Comm.* **1979,** *8,* 69; d) F. Lazarini, *Acta Crystallogr.* **1985,** *C41*, 1144; e) B. Sundvall, *Acta chem.Scand.*, **1979,** *A33*, 219.

[6] A. Ouchi, Y. Susuki, Y. Okhi and Y. Koizumi, *Coord. Chem Rev.* **1988**, *92*, 29.

[7] D.F. Shriver and M.A. Drezdzon, *The Manipulation of Air-sensitive compounds,* 2.Ed., J. Wiley & Sons, New York, **1986**.

[8] Siemens Analytical X-ray Instruments SHELXTL-plus (IRIS), Release 4.2, **1991**.

[9] I. Naringbauer, J.-O. Lundgren and E.K. Andersen, *Acta Crystallogr.* **1979,** *B35,* 508.

[10] L.Pauling, The Nature of the Chemical Bond and the Structure of Molecules and Crystals, 3rd ed., Cornell Press, New York.

[11] I.D. Brown and D. Altermatt *Acta Crystallogr.* **1985,** *B41*, 244.

Received: May 3, 1995 - Accepted: May 22, 1995 - Received revised camera-ready manuscript: June 7, 1995