

Disordered Structure of Polymeric Bismuth Tribenzoate, $[\text{Bi}(\text{C}_6\text{H}_5\text{COO})_3]_n$

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Abstract

Bismuth tribenzoate, $\text{Bi}(\text{C}_6\text{H}_5\text{COO})_3$, was prepared by ligand exchange of bismuth triacetate with benzoic acid. A 1:1 disordered structure of $P2_1/m$ symmetry, $a = 7.858$ (3), $b = 14.442$ (2), $c = 16.807$ (3) Å, $\beta = 92.26$ (2)°, $V = 1906$ (1) Å³, $Z = 4$, consists of polymeric chains parallel to the **a** axis and can be related to an ideally ordered structure of $B2_1/a$ symmetry with $\mathbf{a}' = 2\mathbf{a}$, $\mathbf{b}' = \mathbf{b}$ and $\mathbf{c}' = 2\mathbf{c}$. This *B*-centred structure can itself be described as a modulation of an idealized parent structure of *Pnma* symmetry. The disorder is rationalized in terms of the pseudo-symmetry that relates the two formula units of $\text{Bi}(\text{C}_6\text{H}_5\text{COO})_3$ in the asymmetric unit of $B2_1/a$. In the polymeric chain each Bi atom is nominally nine-coordinate, with widely varying bond lengths arranged in a very asymmetric manner. The polymeric chain is created by each bismuth being chelated to three benzoate ligands. Each such ligand also has one of its O atoms bridging an adjacent Bi atom so that three bridging O atoms link adjacent bismuths. Apparent valences are consistent with expected values for all Bi and O atoms. A final value of 0.0454 was obtained for $R(F)$ using the 1813 independent reflections (out of 2839) with $I(\mathbf{h}) > 3\sigma[I(\mathbf{h})]$ to refine 185 parameters describing 56 non-H atoms.

1. Introduction

Some of our recent work has been involved with the preparation of sol-gel precursors for bismuth-containing ceramics. The title compound was prepared by a simple transesterification reaction using bismuth triacetate in excess hot benzoic acid, removing the liberated acetic acid by distillation. A range of bismuth(III) triesters has been reported using a similar route, although elemental analytical data suggested that the isolated compounds were not pure (Koch & Wickham, 1979).

There are only a few structurally characterized bismuth(III) triesters reported (*e.g.* Reiss *et al.*, 1995).

2. Experimental

The title compound, $\text{C}_{21}\text{H}_{15}\text{BiO}_6$ ($M_r = 572.3$), was prepared by heating bismuth triacetate in excess molten benzoic acid, such that the liberated acetic acid was removed by distillation. Crystals suitable for X-ray crystallography formed on cooling the solution. Excess benzoic acid was removed by washing with ethyl acetate. Analysis: found: C 44.07, H 2.53; calculated C 44.07, H 2.64%.

2.1. Data collection

Preliminary examination and data collection used graphite-monochromated Mo $K\alpha$ X-rays on a Siemens P4 diffractometer at 173 K under flowing nitrogen gas coolant. Cell constants were based on 16 centred reflections in the range $13.0 < 2\theta < 26.3^\circ$ (Fait, 1991). An absorption correction was applied empirically using φ -scan data (Sheldrick, 1985), with minimum and maximum transmission coefficients 0.643 and 0.974, respectively, for a needle-like crystal with dimensions $0.13 \times 0.24 \times 0.55$ mm. Data were collected using the primitive monoclinic cell $a = 7.858$ (3), $b = 14.442$ (2), $c = 16.807$ (3) Å, $\beta = 92.26$ (2)°, $V = 1906$ (1) Å³, $Z = 4$, $D_m = 1.99$ (5) (by density gradient), $D_x = 1.99$ g cm⁻³, $\mu = 9.29$ mm⁻¹. A total of 2935 reflections, including 3 monitoring standards, were collected within the limits $4 < 2\theta < 45^\circ$ ($0 \leq h \leq 8$, $0 \leq k \leq 15$, $-18 \leq l \leq 18$) using conventional ω scans, width 1.24° at 15° min⁻¹. The internal agreement R_{int} was 0.065. Of the 2839 unique reflections, 1813 had $I(\mathbf{h}) > 3\sigma[I(\mathbf{h})]$ (Sheldrick, 1985). There was no crystal decomposition detected during the data collection.

2.2. Structure solution and refinement

Reflection data were collected and indexed in a monoclinic cell, $P2_1/m$, $Z = 4$. The Bi atoms were readily located from a Patterson map. An unambiguous interpretation required that the mirror describes a 1:1 disorder of an ideally ordered structure, giving two half-occupancy Bi atoms in the asymmetric unit. One of these

two Bi atoms lies approximately on the mirror. The eventual interpretation of the structure is that an ideally ordered structure has space-group $B2_1/a$ structure with a larger unit cell, $\mathbf{a}' = 2\mathbf{a}$, $\mathbf{b}' = \mathbf{b}$ and $\mathbf{c}' = 2\mathbf{c}$, and the Fourier transform of the h' even, l' even subset of reflections associated with $B2_1/a$ necessarily has the observed $P2_1/m$ symmetry. A mechanism for the loss of the h' odd, l' odd subset of reflections is part of the structure description. $B2_1/a$ is a non-standard setting of $P2_1/c$.

In the structure description and refinement the fractional coordinates referenced the cell \mathbf{a} , \mathbf{b} , \mathbf{c} and the reflection indices referenced the corresponding reciprocal cell. Consequently, the equivalent positions (modulo $2\mathbf{a}$, \mathbf{b} , $2\mathbf{c}$) of $B2_1/a$ are $(0,0,0$ and $1,0,1+)$ x , y , z ; $1+x$, $\frac{1}{2}-y$, z ; $-x$, $-y$, $-z$; $1-x$, $\frac{1}{2}+y$, $-z$. These are half of the equivalent positions of $P2_1/m$ (modulo $2\mathbf{a}$, \mathbf{b} , $2\mathbf{c}$).

The structure was determined from difference maps of $P2_1/m$ symmetry by choosing between disordered atom sites across the mirror plane. The structure consists of polymeric chains parallel to \mathbf{a} and to avoid close contacts between phenyl rings it was necessary to replace the mirror $x, \frac{1}{2}-y, z$ by the a glide $1+x, \frac{1}{2}-y, z$ and so relate atoms in a polymer chain.

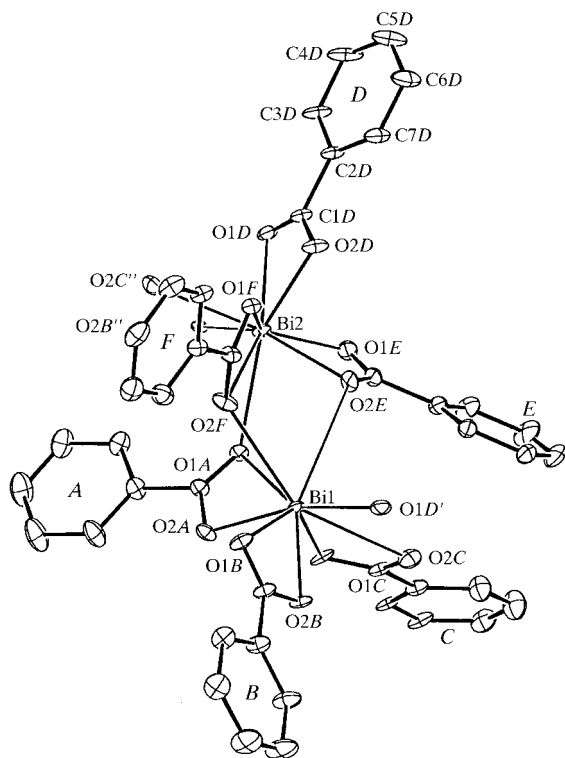


Fig. 1. A generalized view of the repeating unit of the Bi benzoate polymer showing the atom labels and the nine-coordinate Bi environments (30% probability ellipsoids).

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2)

$$U_{\text{eq}} = (U_1^2 U_2^2 U_3^2)^{1/3}.$$

	x	y	z	U_{eq}
Bi1	0.1629 (1)	0.3068 (1)	0.7174 (1)	0.02
Bi2	0.6650 (1)	0.2569 (3)	0.7979 (1)	0.024
O1A	0.4612 (14)	0.249 (3)	0.6597 (6)	0.022 (7)
O2A	0.2699 (17)	0.3502 (12)	0.6044 (7)	0.024 (7)
C1A	0.4178 (13)	0.3096 (10)	0.6131 (5)	0.022 (7)
C2A	0.5341 (11)	0.3334 (7)	0.5443 (5)	0.030 (8)
C3A	0.6979 (14)	0.3000 (10)	0.5434 (8)	0.032 (8)
C4A	0.8046 (17)	0.3208 (12)	0.4818 (9)	0.043 (11)
C5A	0.743 (2)	0.3762 (11)	0.4207 (9)	0.057 (14)
C6A	0.580 (2)	0.4109 (12)	0.4196 (8)	0.058 (14)
C7A	0.4764 (17)	0.3887 (10)	0.4822 (7)	0.043 (11)
O1B	0.0583 (16)	0.4724 (10)	0.7062 (10)	0.030 (5)
O2B	-0.0913 (18)	0.3498 (10)	0.6642 (10)	0.024 (6)
C1B	-0.0669 (13)	0.4375 (8)	0.6762 (8)	0.027 (5)
C2B	-0.2233 (11)	0.4979 (7)	0.6539 (6)	0.034 (7)
C3B	-0.2193 (17)	0.5922 (9)	0.6656 (9)	0.038 (8)
C4B	-0.359 (2)	0.6478 (10)	0.6459 (11)	0.049 (11)
C5B	-0.504 (2)	0.6064 (11)	0.6139 (10)	0.061 (15)
C6B	-0.5126 (16)	0.5123 (12)	0.6014 (11)	0.060 (14)
C7B	-0.3703 (15)	0.4588 (10)	0.6219 (9)	0.043 (10)
O1C	0.1117 (18)	0.1809 (11)	0.6412 (8)	0.031 (5)
O2C	-0.067 (2)	0.1627 (13)	0.7399 (9)	0.035 (7)
C1C	-0.0026 (15)	0.1376 (7)	0.6790 (7)	0.026 (5)
C2C	-0.0295 (11)	0.0354 (6)	0.6555 (5)	0.027 (5)
C3C	0.0332 (16)	0.0011 (9)	0.5860 (7)	0.027 (5)
C4C	0.010 (2)	-0.0909 (10)	0.5639 (9)	0.033 (5)
C5C	-0.0778 (19)	-0.1482 (10)	0.6132 (9)	0.044 (10)
C6C	-0.142 (2)	-0.1163 (9)	0.6830 (10)	0.056 (11)
C7C	-0.1167 (18)	-0.0239 (8)	0.7033 (8)	0.045 (8)
O1D	0.9494 (18)	0.1646 (12)	0.8392 (7)	0.032 (5)
O2D	0.7598 (16)	0.2220 (11)	0.9202 (8)	0.034 (4)
C1D	0.8990 (15)	0.1785 (9)	0.9053 (5)	0.026 (5)
C2D	0.9992 (12)	0.1418 (7)	0.9794 (5)	0.029 (7)
C3D	1.1574 (16)	0.1023 (11)	0.9728 (8)	0.041 (10)
C4D	1.2496 (18)	0.0688 (12)	1.0390 (10)	0.056 (14)
C5D	1.179 (2)	0.0759 (11)	1.1124 (9)	0.058 (15)
C6D	1.021 (2)	0.1150 (13)	1.1212 (7)	0.057 (13)
C7D	0.9327 (17)	0.1477 (11)	1.0537 (6)	0.041 (8)
O1E	0.5779 (17)	0.0987 (11)	0.8052 (9)	0.031 (4)
O2E	0.4047 (18)	0.2101 (8)	0.8411 (10)	0.034 (5)
C1E	0.4396 (15)	0.1248 (7)	0.8291 (8)	0.027 (3)
C2E	0.2972 (13)	0.0574 (6)	0.8515 (5)	0.028 (3)
C3E	0.3114 (18)	-0.0360 (8)	0.8371 (9)	0.040 (4)
C4E	0.184 (2)	-0.0979 (9)	0.8569 (11)	0.055 (8)
C5E	0.0415 (19)	-0.0637 (11)	0.8917 (9)	0.054 (9)
C6E	0.0231 (17)	0.0293 (13)	0.9070 (10)	0.044 (8)
C7E	0.1529 (16)	0.0892 (9)	0.8864 (8)	0.032 (5)
O1F	0.6237 (17)	0.3860 (11)	0.8756 (7)	0.022 (4)
O2F	0.455 (2)	0.4074 (13)	0.7711 (8)	0.039 (7)
C1F	0.5212 (16)	0.4311 (8)	0.8312 (7)	0.026 (4)
C2F	0.5154 (11)	0.5353 (7)	0.8507 (5)	0.028 (5)
C3F	0.5903 (17)	0.5691 (9)	0.9202 (7)	0.029 (5)
C4F	0.586 (2)	0.6629 (10)	0.9388 (9)	0.040 (8)
C5F	0.5051 (19)	0.7223 (10)	0.8858 (9)	0.046 (10)
C6F	0.429 (2)	0.6909 (9)	0.8158 (10)	0.047 (10)
C7F	0.4353 (17)	0.5967 (8)	0.7991 (8)	0.040 (8)

The space group $B2_1/a$ is a consequence of the packing of such chains and this space group is the only option that allows a feasible packing arrangement, consistent with a selection of half the symmetry

Table 2. Selected geometric parameters (\AA , $^\circ$)

Bi1—O1A	2.704 (16)	Bi2—O1D	2.670 (16)
Bi1—O2A	2.198 (14)	Bi2—O2D	2.217 (14)
Bi1—O1B	2.533 (16)	Bi2—O1E	2.390 (18)
Bi1—O2B	2.243 (14)	Bi2—O2E	2.300 (15)
Bi1—O1C	2.251 (14)	Bi2—O1F	2.307 (16)
Bi1—O2C	2.793 (18)	Bi2—O2F	2.755 (18)
Bi1—O1D ⁱ	2.729 (10)	Bi2—O1A	2.770 (11)
Bi1—O2E	3.095 (14)	Bi2—O2B ⁱⁱ	3.380 (16)
Bi1—O2F	2.833 (13)	Bi2—O2C ⁱⁱ	2.624 (16)
C1A—O1A	1.21 (3)	C1D—O1D	1.210 (11)
C1A—O2A	1.304 (15)	C1D—O2D	1.294 (16)
C7A—C6A	1.391 (11)	C1E—O1E	1.232 (15)
C1B—O1B	1.199 (10)	C1E—O2E	1.279 (12)
C1C—O1C	1.283 (13)	C1F—O1F	1.258 (13)
C1C—O2C	1.216 (9)	C1F—O2F	1.169 (12)
C2n—C1n [†]	1.541 (8)	C3n—C2n [†]	1.376 (8)
C4n—C3n [†]	1.391 (11)	C5n—C4n [†]	1.376 (10)
C6A—C7A ⁱⁱⁱ	3.371 (31)	C2D—C4D ^{iv}	3.623 (24)
C7A—C7A ⁱⁱⁱ	3.290 (30)	O2D—O1F ^v	2.018 (19)
O1A—Bi1—O2A	54.0 (6)	O1D—Bi2—O2D	53.0 (4)
O1B—Bi1—O2B	55.1 (4)	O1E—Bi2—O2E	56.1 (4)
O1C—Bi1—O2C	51.2 (4)	O1F—Bi2—O2F	50.1 (4)
O1A—Bi1—O1B	123.2 (9)	O1D—Bi2—O1E	75.4 (5)
O1A—Bi1—O2B	135.5 (5)	O1D—Bi2—O2E	121.1 (5)
O1A—Bi1—O1C	71.6 (8)	O1D—Bi2—O1F	113.0 (4)
O1A—Bi1—O2C	113.2 (9)	O1D—Bi2—O2F	157.8 (5)
O2A—Bi1—O1B	78.5 (6)	O2D—Bi2—O1E	79.7 (6)
O2A—Bi1—O2B	86.7 (5)	O2D—Bi2—O2E	84.9 (5)
O2A—Bi1—O1C	78.7 (5)	O2D—Bi2—O1F	73.0 (5)
O2A—Bi1—O2C	127.0 (5)	O2D—Bi2—O2F	120.5 (5)
O1B—Bi1—O1C	132.1 (5)	O1E—Bi2—O1F	134.1 (5)
O1B—Bi1—O2C	120.3 (5)	O1E—Bi2—O2F	126.3 (4)
O2B—Bi1—O1C	82.0 (5)	O2E—Bi2—O1F	84.9 (5)
O2B—Bi1—O2C	71.9 (5)	O2E—Bi2—O2F	175.5 (5)
O1A—Bi1—O1D ⁱ	152.0 (4)	O1A—Bi2—O1D	130.3 (7)
O1A—Bi1—O2E	65.4 (4)	O1D—Bi2—O2B ⁱⁱ	57.0 (3)
O1A—Bi1—O2F	64.5 (7)	O1D—Bi2—O2C ⁱⁱ	69.1 (5)
O2A—Bi1—O1D ⁱ	150.8 (5)	O1A—Bi2—O2D	158.4 (7)
O2A—Bi1—O2E	117.6 (4)	O2D—Bi2—O2B ⁱⁱ	109.5 (4)
O2A—Bi1—O2F	78.3 (5)	O2D—Bi2—O2C ⁱⁱ	101.5 (5)
O1B—Bi1—O1D ⁱ	72.9 (5)	O1A—Bi2—O1E	81.2 (9)
O1B—Bi1—O2E	131.7 (4)	O1E—Bi2—O2B ⁱⁱ	76.7 (4)
O1B—Bi1—O2F	78.2 (4)	O1E—Bi2—O2C ⁱⁱ	132.7 (5)
O2B—Bi1—O1D ⁱ	72.1 (5)	O1A—Bi2—O2E	76.2 (5)
O2B—Bi1—O2E	155.0 (5)	O2E—Bi2—O2B ⁱⁱ	127.6 (5)
O2B—Bi1—O2F	133.0 (5)	O2E—Bi2—O2C ⁱⁱ	169.7 (5)
O1C—Bi1—O1D ⁱ	116.6 (5)	O1A—Bi2—O1F	114.8 (8)
O1C—Bi1—O2E	96.2 (5)	O1F—Bi2—O2B ⁱⁱ	147.2 (5)
O1C—Bi1—O2F	136.0 (5)	O1F—Bi2—O2C ⁱⁱ	89.2 (5)
O2C—Bi1—O1D ⁱ	65.8 (5)	O1A—Bi2—O2F	64.7 (8)
O2C—Bi1—O2E	87.5 (5)	O2F—Bi2—O2B ⁱⁱ	127.1 (4)
O2C—Bi1—O2F	149.2 (5)	O2F—Bi2—O2C ⁱⁱ	94.3 (6)
O2E—Bi1—O2F	63.2 (4)	O2B ⁱⁱ —Bi2—O2C ⁱⁱ	58.1 (5)
O2E—Bi1—O1D ⁱ	86.7 (4)	O1A—Bi2—O2B ⁱⁱ	75.4 (5)
O2F—Bi1—O1D ⁱ	101.4 (5)	O1A—Bi2—O2C ⁱⁱ	98.8 (6)
Bi1—O1A—C1A	77.4 (10)	Bi2—O1D—C1D	81.7 (9)
Bi1—O2A—C1A	98.3 (7)	Bi2—O2D—C1D	100.7 (7)
Bi1—O1B—C1B	83.8 (8)	Bi2—O1E—C1E	88.9 (8)
Bi1—O2B—C1B	94.9 (8)	Bi2—O2E—C1E	91.9 (8)
Bi1—O1C—C1C	103.0 (7)	Bi2—O1F—C1F	100.5 (8)
Bi1—O2C—C1C	79.2 (9)	Bi2—O2F—C1F	81.1 (9)
Bi1 ⁱⁱ —O1D—C1D	153.7 (12)	Bi2—O1A—C1A	131 (2)
Bi1—O2E—C1E	117.3 (10)	Bi2 ⁱ —O2B—C1B	115.3 (10)
Bi1—O2F—C1F	138.9 (13)	Bi2 ⁱ —O2C—C1C	144.3 (13)
Bi1—O1A—Bi2	99.6 (5)	Bi1 ⁱⁱⁱ —O1D—Bi2	105.2 (5)
Bi1—O2B—Bi2 ⁱ	97.4 (5)	Bi1—O2E—Bi2	100.6 (5)
Bi1—O2C—Bi2 ⁱ	104.7 (6)	Bi1—O2F—Bi2	96.9 (5)

Table 2. (cont.)

O1A—C1A—O2A	128.5 (12)	O1C—C1C—O2C	126.6 (13)
O1A—C1A—C2A	119.0 (8)	O1C—C1C—C2C	115.5 (8)
O2A—C1A—C2A	111.5 (8)	O2C—C1C—C2C	116.3 (10)
O1B—C1B—O2B	126.2 (13)	O1E—C1E—O2E	123.0 (13)
O1B—C1B—C2B	119.8 (10)	O1E—C1E—C2E	122.9 (9)
O2B—C1B—C2B	113.8 (8)	O2E—C1E—C2E	114.0 (9)
O1D—C1D—O2D	124.6 (12)	O1F—C1F—O2F	127.9 (15)
O1D—C1D—C2D	120.6 (10)	O1F—C1F—C2F	113.7 (9)
O2D—C1D—C2D	114.8 (7)	O2F—C1F—C2F	117.0 (11)

[†] Benzoate ligands ($n = A, B, C, D, E$ and F ; $2mm$ ring symmetry. Symmetry codes: (i) $-1 + x, \frac{1}{2} - y, z$; (ii) $1 + x, \frac{1}{2} - y, z$; (iii) $1 - x, 1 - y, 1 - z$; (iv) $2 - x, -y, 2 - z$; (v) $x, \frac{1}{2} - y, z$.

elements of $P2_1/m$. The lack of an alternative packing arrangement creates a difficulty for explaining the non-observation of the extra reflections expected for $B2_1/a$. A likely explanation is given later.

2.3. Structure refinement

The structure was refined using *RAEL596* (Rae, 1996b; see also Rae, 1975; Haller *et al.*, 1995). The Bi atoms were refined as isolated anisotropic atoms, but the benzoate atoms were refined using various constraints and restraints. The same set of refinable localized orthogonal coordinates was used for the seven C atoms of each of the six benzoate rings, a constrained refinement of local x and y coordinates maintaining a local $2mm$ symmetry. The locations and orientations of these rings were also refined. The O atoms were not constrained by these local symmetries, but were restrained so that the apparent valences (Brown & Altermatt, 1985; Brese & O'Keeffe, 1991) of the O atoms approached equality within the same ligand and between the pseudo-related pairs (*AD*, *BE* and *CF*). An equality restraint was also placed on the apparent valences of Bi. This enabled resolution of the Bi2 and O1A atoms which lie effectively on the disordering mirror plane. The final apparent valences for Bi were both 3.08 and ranged between 1.97 and 2.01 for O. H atoms were included in chemically sensible positions after each refinement cycle. The thermal parameters of the benzoates were refined assuming rigid-body motion, each group having its own set of 15 *TLX* parameters. The 1:1 disorder causes ligands *B* and *C*, and *E* and *F* to overlap. The *T* matrices were slightly non-positive definite in some instances, but not so as to be statistically significant in a refinement dominated by the Bi contributions.

The refinement used 185 parameters for 56 non-H atoms and the 1813 independent reflections

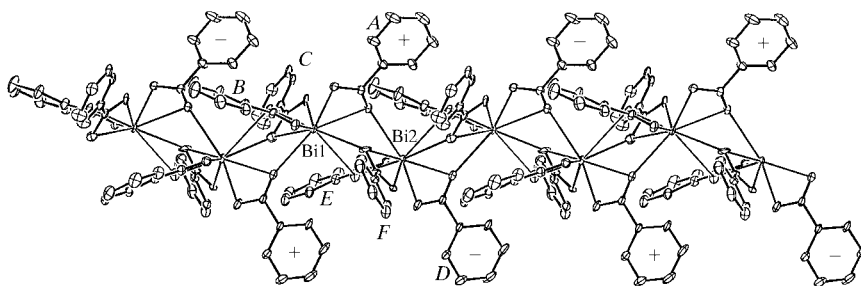


Fig. 2. A projection down **b** of a polymer chain of the ordered $B2_1/a$ structure (30% probability ellipsoids). Adjacent asymmetric units are related by the *a* glide. A mirror perpendicular to **b** creates a 1:1 disordered structure with space group $P2_1/m$ with a smaller unit cell and approximate $Pnma$ symmetry. The pseudo-symmetry operations relate Bi1 and ligands *A*, *B* and *C* to Bi2 and ligands *D*, *E* and *F*, and allow a mechanism for the observed disorder (see text).

(out of 2839) with $I(\mathbf{h}) > 3\sigma[I(\mathbf{h})]$ gave final values of

$$R(F) = \frac{\sum_{\mathbf{h}} |\Delta F_{\mathbf{h}}|}{\sum_{\mathbf{h}} |\Delta F_{\mathbf{h}}|} = 0.0454R(F^2)$$

$$R(F^2) = \frac{\sum_{\mathbf{h}} |\Delta(F_{\mathbf{h}}^2)|}{\sum_{\mathbf{h}} |F_{\mathbf{h}}^2|} = 0.0749$$

$$wR = \left[\frac{\sum_{\mathbf{h}} w_{\mathbf{h}} |\Delta F_{\mathbf{h}}|^2}{\sum_{\mathbf{h}} w_{\mathbf{h}} |F_{\mathbf{h}}^2|} \right]^{1/2}$$

$$\text{g.o.f.} = 0.0505 \left[\frac{\sum_{\mathbf{h}} w_{\mathbf{h}} |\Delta F_{\mathbf{h}}|^2}{(n - m)} \right]^{1/2} = 1.38.$$

An uncorrelated 2% error in *F* was included in the estimation of errors for evaluating the weighting scheme.

3. Description of the structure

Fractional coordinates are given in Table 1. The labelling of the atoms in an asymmetric unit is given in Fig. 1, which shows a generalized view of the repeating unit of the Bi benzoate polymer. A projection down **b** of the polymer chain along **a** is shown in Fig. 2. Bond lengths and angles are given in Table 2.†

Each Bi atom has eight Bi—O bonds less than 2.85 Å and one longer Bi—O contact, which is still within the sum of the van der Waals radii (3.67 Å; Alcock, 1972). Such variable ninefold coordination has been noted previously in a bismuth trifluoroacetate adduct (Reiss *et al.*, 1995). As verified in Table 2 and seen in Fig. 1, the angular distributions of O atoms around Bi1 and Bi2 are not the same. The asymmetric environment of the Bi atoms cannot be approximated to idealized geometries (Rogers *et al.*, 1992), even though some elements are present; for example, atoms O2*B*, O1*B*, O1*C*, O2*F* and O1*A* form an approximately pentagonal face with respect to Bi1. The uncoordinated region in Bi1 is associated with a lone pair of electrons and is well known for Bi atoms (see Breeze & Wang, 1993; Breeze *et al.*, 1994; Barton *et al.*, 1984).

† Lists of atomic coordinates, anisotropic displacement parameters and structure factors have been deposited with the IUCr (Reference: MU0326). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

For ligands *A*, *B* and *C* both O atoms are coordinated to Bi1, while one oxygen per ligand (O1*A*, O2*B*, O2*C*) is coordinated to an adjacent Bi2 atom. Somewhat similarly, both O atoms for ligands *D*, *E* and *F* are coordinated to Bi2 and one oxygen per ligand (O2*E*, O2*F* and O1*D*) is bound to an adjacent Bi1 atom. There are three bridging O atoms between every Bi in a chain, one bridging contact being long. In both cases the longer bridging bonds (to O2*B* and O2*E*) are associated with shorter distances for the remaining Bi—O contacts: *e.g.* Bi1—O2*E* 3.10 (1), Bi2—O1*E* 2.39 (2) Å. The C—O bond lengths for O atoms involved in longer Bi—O bonds (> 2.53 Å) are shorter than the others [averages 1.20 (1) and 1.28 (1) Å, respectively], as observed previously (Bensch *et al.*, 1987). Fig. 2 shows that atoms in ligands *A*, *B* and *C* have *z* coordinates between $\frac{1}{2}$ and $\frac{3}{4}$, while atoms in the pseudo-symmetry-related ligands *D*, *E* and *F* have *z* coordinates between $\frac{3}{4}$ and 1 and are on the opposite side of $z = \frac{3}{4}$.

4. Explanation for the missing reflections

The structure can be interpreted as being a perturbation away from the parent structure of $Pnma$ symmetry, with a cell of dimensions *a*, *b* and *c*. The ordered $B2_1/a$ structure is then described as a modulated structure with a doubly degenerate irreducible representation being associated with the modulation vector $(\mathbf{a}^* + \mathbf{c}^*)/2$. More correctly, the bases for two time-reversal symmetry-linked one-dimensional irreducible representations are combined in equal amounts (Bradley & Cracknell, 1972) and β changes from 90 to 92.26°. Refinement problems associated with twinning and disorder often occur in this type of structure (Rae, 1996*a*).

The perturbation associated with the modulation vector $(\mathbf{a}^* + \mathbf{c}^*)/2$ necessarily destroys the screw axis parallel to **a** ($\frac{1}{2} + x, \frac{1}{2} - y, \frac{3}{2} - z$) and the *a* glide perpendicular to **c*** ($\frac{1}{2} + x, y, \frac{3}{2} - z$), since their repeated operation creates a translation along **a** and this is no longer a symmetry element. However, these symmetry elements become pseudo-symmetry elements and $\frac{1}{2} + x$,

$\frac{1}{2} - y, \frac{3}{2} - z$ approximately relates Bi1 to Bi2, and ligands *A*, *B* and *C* to *D*, *E* and *F*, respectively, and $\frac{1}{2} + x, y, \frac{3}{2} - z$ approximately relates Bi2 and ligands *D*, *E* and *F* to the equivalent positions of Bi1 and ligands *A*, *B* and *C* obtained using the true symmetry operation $1 + x, \frac{1}{2} - y, z$.

Extension of this idea provides an explanation for the non-observation of the extra reflections associated with such a modulation wave. The choice of space group $B2_1/a$ for an ordered structure is based on packing layers (perpendicular to \mathbf{c}^*) of polymeric chains parallel to \mathbf{a} and of particular importance are the actual positions of ligands *A* and *D*. Let us consider the reference layer at $z = \frac{3}{4}$.

If the pseudo-symmetry operator $\frac{1}{2} + x, \frac{1}{2} - y, \frac{3}{2} - z$ acts as a real operator on this layer, then ligands *A*, *B* and *C* take up the positions previously held by ligands *D*, *E* and *F*, and ligands *D*, *E* and *F* take up positions \mathbf{a} translated relative to the previous positions of ligands *A*, *B* and *C*. Thus, one side of the layer at $z = \frac{3}{4}$ looks essentially unchanged, while the other side appears to be translated by \mathbf{a} . Thus, such an interfacial layer allows the structure on one side of the layer to remain unchanged, while the structure on the other side of the layer translates by \mathbf{a} , giving an average structure of $P2_1/m$ symmetry for the limiting case where there is an equal probability of origins \mathbf{a} apart. The adjustments available from the flexible coordination geometry of Bi makes this a reasonable explanation.

Note. Table 2 contains some short contacts. Equivalent positions (iii) $1 - x, 1 - y, 1 - z$ and (iv) $2 - x, -y, 2 - z$ indicate allowed symmetry elements. The operator (v) $x, \frac{1}{2} - y, z$ is the disordering mirror and the contact $\text{O}2\text{D} - \text{O}1\text{F}^v$ of 2.02 (2) Å would have to be acceptable

for the polymeric chain to have a repeat of \mathbf{a} rather than $2\mathbf{a}$.

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