X-Ray Studies on Bismuth Oxide Acetate CH₃COO·OBi and Related Compounds

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Bismuth oxide acetate and a series of compounds of approximate composition R-COO-OBi have been prepared. The general arrangement of the atoms seems to be the same as that for BiOCl, the organic anions replacing the chloride ions. A tentative structure is given for the oxide acetate.

The bismuth oxide salts of various fatty acids were prepared using a procedure similar to that given by Hofmann 1 for the synthesis of bismuth oxide acetate. Bismuth oxide was dissolved in the proper acid, the solution diluted with water and the excess acid distilled off. In this way it was possible to synthesize pure specimens of the bismuth oxide salt of acetic acid. Corresponding syntheses of the formate, propionate, n-butyrate and n-valerate were also performed and gave samples with somewhat high contents of bismuth when compared with the ideal formula of $R \cdot COO \cdot OBi$. The propionate samples were found to belong to a phase of an extended homogeneity range (vide infra). The n-butyrate and n-valerate were not investigated from this point of view (cf. Table 1). The formate and the acetate were obtained as very thin crystal plates. The former was generally discoloured by reduced bismuth while the latter was colourless. The other salts were white powders.

X-ray powder photographs of the various preparations were taken in a Guinier focusing camera using $\text{Cu-}K\alpha$ radiation. Parts of the powder photographs of the formate, acetate, propionate, and *n*-butyrate are given in Table 2.

Table 1. Analysis for Bi₂O₃. Observed and calculated densities.

Compound	% Bi ₂ O ₃ obs.	% Bi ₂ O ₃ calc.	Density obs.	Density calc.
$BiO \cdot OOCH$	88.8	86.3	6.0	5.82
$BiO \cdot OOCCH_3$	81.6	82.0	4.7	4.72
BiO · OOCC ₂ H ₅	80.6	78.2	4.1	4.40
BiO · OOCC ₃ H ₇	77.8	74.7	3.7	3.93
BiO · OOCC4H,	73.6	71.4		3.56

Table 2. Part of the powder photographs of bismuth oxide formate, acetate, propionate and n-butyrate.

Bismuth oxide formate

I obs	104sin2 9 obs	104sin2 0 calc	hkl	I obs	104sin20 obs	104sin20 calc	hkl
\mathbf{m}	58	58	001	vw	683	-	
\mathbf{m}	451	451	101	vvw	750		
w	522	520	003	\mathbf{m}	787	785	110
vw	555		_	\mathbf{w}	845	843	111
st	629	624	102	w	914	911	103
	Bismu	th oxide ac	etate.	Pseudo-tetro	agonal des	scription.	
m	36	37	001	vw	922	924	005
vw	148	148	002	vw	951		_
$\operatorname{\mathbf{st}}$	416	415	101	vw	969	969	104
vst	523	526	102	vw-	1 091	1 088	113
vw	601	591	004	_			_
\mathbf{st}	709	711	103	w	3 014)	0.000	200
\mathbf{st}	753	755	110	w	3 034	3 020	220
st	790	792	111	m	3 773		010
vw	904	903	112	m	3 788}	3 775	310
		Bismuth oxi		rionate (80		•	
vst	26	27	001	st	784	787	110
m	106	107	002	\mathbf{m}	812	814	111
\mathbf{w}	419	421	101	\mathbf{m}	828	821	104
$\mathbf{v}\mathbf{w}$	425	427	004	w'	896	894	112
st	502	501	102	w	967	962	006
st	637	635	103	w	1 058	1~062	105
w	670	668	005				
		Bis	muth o	xide n-buty	<i>jrate</i>		
st	20	20	001	\mathbf{m}	637		-
\mathbf{st}	78	78	002	vw	668		
w	175 ·	176	003	m	703	706	006
vw	312	314	004	vw	721		_
$\mathbf{v}\mathbf{w}$	410	_		st	788	792	110
\mathbf{m}	443			vw	815		
vw	447	.—		$\mathbf{v}\mathbf{w}$	835		
\mathbf{w}	477			vw	896	_	
w	487	490	005	vw	954	960	007
\mathbf{m}	520			vw	987	_	-
$\mathbf{v}\mathbf{w}$	540	-		vw	1 048		٠ ـــــ
$\mathbf{v}\mathbf{w}$	580	_	_				

The powder photographs of the salts of formic, acetic and propionic acids could be completely interpreted by assuming tetragonal or pseudo-tetragonal unit cells with $a \sim 3.9$ Å and c-axes increasing from the formate to the propionate (cf. Table 3). In the powder photograph of the acetate most of the lines hkl (h and $k \neq 0$) were found to be doubled. No corresponding splitting up of the lines could be detected in the powder photographs of the formate and propionate. The cell dimensions of the propionate were found to vary with its

Table 3.	Cell	dimensions,	bismuth	parameters	and	distances	within	the	$Bi_{2}O_{2}^{2+}$	layers.	
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Compound	a Å	c Å	V Å3	$z_{ m Bi}$	Height of the Bi atom above $z = 0$	
BiO · OOCH BiO · OOCCH ₃ BiO · OOCC ₂ H ₅ BiO · OOCC ₃ H ₇ * BiO · OOCC ₄ H ₈ *	3.89	10.16	154	0.12_4^{1}	1.26 Å	
	3.97	12.68	200	0.10_0^{1}	1.27	
	3.89	14.92	225	0.08_3^{2}	1.24	
	3.9	17.4	264	0.07_0^{3}	1.22	
	3.9	20.0	304	0.06_3^{3}	1.26	

1) Calculated from Weissenberg photographs.

3) Calculated from powder photographs, 00l row.

content of bismuth. Thus, for a sample with 81.8 % $\rm Bi_2O_3$ the dimensions were a=3.88 Å and c=14.78 Å and for a sample with 80.6 % $\rm Bi_2O_3$ a=3.89 Å and c=14.92 Å.

The powder pattern of the n-butyrate was considerably more complicated than those of the lower fatty acid salts. Some of the lines appeared to be grouped in multiplets (cf. Table 2). However, the majority of the lines of major intensity could also here be accounted for as hk0 or 00l reflexions from a basic unit cell of tetragonal symmetry with a=3.9 Å and c=17.4 Å. Attempts to perform a complete interpretation of the diagram have been without success. The real unit cell may be a distorted modification of the tetragonal unit or it may be a multiple of it. Some of the extra lines may of course be due to impurities.

The *n*-valerate pattern was less complicated than that of the *n*-butyrate and could only be observed up to *d*-values of about 1.36 Å. All except some weak lines could be interpreted as hk0 and 00l reflexions from a tetragonal unit cell of dimensions a = 3.9 Å and c = 20.0 Å.

The conformity of the tetragonal basic unit cells suggests a structural analogy between the various compounds. The density determinations (cf. Table 1) are in agreement with a cell content of two formula units of R·COO·OBi. A similar structural unit has previously been observed for bismuth oxide chloride BiOCl² of PbFCl-type, the structure of which may be described as follows:

Space-group P4/nmm (No. 129)

2 O at 2(a):
$$0,0,0$$
; $\frac{1}{2},\frac{1}{2},0$
2 Bi at 2(c): $0,\frac{1}{2},z$; $\frac{1}{2},0,\overline{z}$ $z = 0.171$
2 Cl at 2(c): $0,\frac{1}{2},z$; $\frac{1}{2},0,\overline{z}$ $z = 0.650$

It seemed worth-while to investigate whether a similar atomic arrangement was present in the present compounds.

Weissenberg photographs ($h0\bar{l}$ and h1l) were taken of a crystal of the bismuth oxide formate using Cu- $K\alpha$ radiation. The Laue symmetry was found to

²⁾ Calculated from powder photographs of a sample of 80.6 % bismuth content.

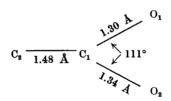
^{*} Dimensions given correspond to 00l and hk0 reflexions.

be 4/mmm. The only systematically absent spectra were hk0 with h+k= odd, which is consistent with the space-group P4/nmm (No. 129). Weissenberg photographs of the acetate showed the same symmetry. The only position for the two bismuth atoms in this space-group, consistent with the observed intensities, is in 2(c). The values for the corresponding z parameters of the various compounds are given in Table 3. The Bi-O distances, assuming 2 oxygen atoms to be situated at 2(a), agree well with those found for the BiO layers in other bismuth oxide compounds 3.

The dominating contribution of the bismuth atoms to the intensities of the reflexions makes the determination of the positions of the light atoms an extremely difficult task. Consequently no attempts were made to solve this problem. However, from a knowledge of the cell dimensions and the positions of the bismuth atoms, the following might be inferred:

From space considerations, it is possible to find positions of the organic anions analogous to the chlorine atom positions in bismuth oxide chloride, the anions thus forming double layers interleaving the layers of $\mathrm{Bi}_2\mathrm{O}_2^{2+}$. Because of electrostatic reasons, it can be assumed that the carboxyl groups are directed towards the $\mathrm{Bi}_2\mathrm{O}_2^{2+}$ layers. However, several alternatives present themselves and so far it is not possible to decide which is the correct one.

As mentioned above the reflexions hkl (h and $k \neq 0$) were found to be doubled in the powder photograph of the oxide acetate. The two lines of the doublets were always of the same intensity. This effect could be accounted for by assuming a monoclinic unit cell with a=c=3.967 Å, b=12.68 Å and $\beta=90.^{\circ}16$ and the symmetry $P\ 2/n$ (no. 13). The corresponding axes for the pseudo-tetragonal cell are a=3.967 Å and c=12.68 Å. A possible atomic arrangement of bismuth oxide acetate consistent with this symmetry is illustrated in Fig. 1. The model for the acetate ion applied here was obtained from the study of zinc acetate dihydrate by v. Niekerk $et\ al.^4$, viz.



The same distances and angles were used here except for the distances $(O_1,O_2)-C_1$ which were assumed to be 1.34 Å. With the monoclinic unit cell and symmetry derived above the Bi atoms would occupy the position 2(e): $\frac{1}{4},y,\frac{1}{4}$; $\frac{3}{4},\overline{y},\frac{3}{4}$ with y=0.10 and the two O atoms of the Bi₂O₂-layers would be situated in 2(f): $\frac{3}{4},y,\frac{1}{4};\frac{1}{4},\overline{y},\frac{3}{4}$ with y=0. The two C₁ and C₂ atoms are supposed to lie on the lines $\frac{1}{4},y,\frac{1}{4};\frac{3}{4},\overline{y},\frac{3}{4}$ (i. e. at the point positions 2(e)) and the $4(O_1,O_2)$ atoms to occupy the position 4(g): $\pm (xyz)$; $\pm (\frac{1}{2}-x,y,\frac{1}{2}-z)$. These latter atoms might either be ordered with for instance x=z=0.05 as pictured in Fig.1 or they might be randomly distributed over a series of positions 4(g) with $(x-\frac{1}{4})^2+(z-\frac{1}{4})^2=(1.11/a)^2$ (1.11 being half the distance O_1-O_2 within an acetate ion and a=c). In the latter case the problem of the orientation of the

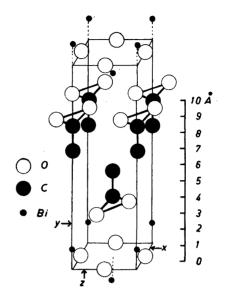


Fig. 1. Tentative structure of bismuth oxide acetate. The origin used in the figure corresponds to the point \$\frac{1}{4}, \theta, \frac{1}{4}\$ in the monoclinic cell described in the text.

carboxyl groups is similar to the problem of the arrangement of the carbonate ions of the minerals bismuthite $(\mathrm{Bi}_2\mathrm{O}_2\mathrm{CO}_3)$ and beyerite $(\mathrm{CaBi}_2\mathrm{O}_2(\mathrm{CO}_3)_2)$, treated by Lagercrantz and Sillén ⁵. The space available requires that the mutual orientation of neighbouring carboxyl groups is ordered while the long range arrangement is a random one. The structures obtained in this way correspond throughout to reasonable interatomic distances, viz. Bi— $\mathrm{O}_{\mathrm{carboxyl}}=2.4$ Å for the ordered alternative and 2.4—2.7 Å for the random one while C—C (of the same layer) = 3.97 Å and C—C (of adjacent layers) = 3.6 Å.

It must in this connection be emphasized that the observed symmetry and cell dimensions may be only those of the arrangement of the heavy bismuth atoms, while the actual symmetry of the structures may be lower and the true unit cell larger.

The area available for one RCOO⁻ group is small, being only about 15 Å² as compared with the value 18.2—18.9 Å² obtained for potassium soaps (angle of tilt 53—55°) by Lomer ⁶, the value 17.4 Å² obtained by Vand, Aitken and Campbell ⁷ for silver caproate at 20° C (angle of tilt 73°), both determined by X-ray methods, and the value 21 Å² obtained from surface measurements by Langmuir ⁸ and several other investigators. All of the latter data refer to fairly long chain molecules and it is interesting to note that attempts to prepare bismuth oxide salts of fatty acids higher than n-valeric acid and also of iso-acids have been without success, and that the syntheses of the n-butyrate and n-valerate were found to be rather troublesome. It is obvious that only the short chain acids are able to accomodate themselves easily to the restricted mesh of the $\text{Bi}_2\text{O}_2^{2+}$ layers. A possibility which has not so far been tested is that hydroxyl groups are substituted for a minor proportion of the fatty acid anions of, e. g., the propionate. This arrangement would give a more probable area per fatty acid ion and account for the fact that the unit cells of these

compounds are different from those of the lower fatty acid salts. This hypothetical substitution mechanism might also explain the variable composition and unit cell dimensions observed for the propionate.

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