

X-Ray Studies on Bismuth Oxide Acetate $\text{CH}_3\text{COO}\cdot\text{OBi}$ and Related Compounds

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Bismuth oxide acetate and a series of compounds of approximate composition $\text{R}\cdot\text{COO}\cdot\text{OBi}$ 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 Hofmann¹ 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 $\text{R}\cdot\text{COO}\cdot\text{OBi}$. 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 $\text{Cu}\cdot\text{K}\alpha$ radiation. Parts of the powder photographs of the formate, acetate, propionate, and *n*-butyrate are given in Table 2.

Table 1. Analysis for Bi_2O_3 . Observed and calculated densities.

Compound	% Bi_2O_3 obs.	% Bi_2O_3 calc.	Density obs.	Density calc.
$\text{BiO}\cdot\text{OOCH}$	88.8	86.3	6.0	5.82
$\text{BiO}\cdot\text{OOCCH}_3$	81.6	82.0	4.7	4.72
$\text{BiO}\cdot\text{OOCCH}_2\text{H}_5$	80.6	78.2	4.1	4.40
$\text{BiO}\cdot\text{OOCCH}_2\text{H}_7$	77.8	74.7	3.7	3.93
$\text{BiO}\cdot\text{OOCCH}_2\text{H}_9$	73.6	71.4		3.56

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

<i>Bismuth oxide formate</i>							
<i>I</i> obs	$10^4 \sin^2 \Theta$ obs	$10^4 \sin^2 \Theta$ calc	<i>hkl</i>	<i>I</i> obs	$10^4 \sin^2 \Theta$ obs	$10^4 \sin^2 \Theta$ calc	<i>hkl</i>
m	58	58	001	vw	683	—	—
m	451	451	101	vvw	750	—	—
w	522	520	003	m	787	785	110
vw	555	—	—	w	845	843	111
st	629	624	102	w	914	911	103
<i>Bismuth oxide acetate. Pseudo-tetragonal description.</i>							
m	36	37	001	vw	922	924	005
vw	148	148	002	vw	951	—	—
st	416	415	101	vw	969	969	104
vst	523	526	102	vw—	1 091	1 088	113
vw	601	591	004	—	—	—	—
st	709	711	103	w	3 014	3 020	220
st	753	755	110	w	3 034		
st	790	792	111	m	3 773	3 775	310
vw	904	903	112	m	3 788		
<i>Bismuth oxide propionate (80.6 % Bi₂O₃)</i>							
vst	26	27	001	st	784	787	110
m	106	107	002	m	812	814	111
w	419	421	101	m	828	821	104
vw	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				
<i>Bismuth oxide n-butyrate</i>							
st	20	20	001	m	637	—	—
st	78	78	002	vw	668	—	—
w	175	176	003	m	703	706	006
vw	312	314	004	vw	721	—	—
vw	410	—	—	st	788	792	110
m	443	—	—	vw	815	—	—
vw	447	—	—	vw	835	—	—
w	477	—	—	vw	896	—	—
w	487	490	005	vw	954	960	007
m	520	—	—	vw	987	—	—
vw	540	—	—	vw	1 048	—	—
vw	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 $\text{Bi}_2\text{O}_3^{2+}$ layers.

Compound	a Å	c Å	V Å ³	z_{Bi}	Height of the Bi atom above $z = 0$
$\text{BiO} \cdot \text{OOCH}$	3.89	10.16	154	0.12 ₄ ¹⁾	1.26 Å
$\text{BiO} \cdot \text{OOCCH}_3$	3.97	12.68	200	0.10 ₀ ¹⁾	1.27
$\text{BiO} \cdot \text{OOCCH}_2\text{H}_5$	3.89	14.92	225	0.08 ₃ ²⁾	1.24
$\text{BiO} \cdot \text{OOCCH}_2\text{H}_7^*$	3.9	17.4	264	0.07 ₀ ³⁾	1.22
$\text{BiO} \cdot \text{OOCCH}_4\text{H}_9^*$	3.9	20.0	304	0.06 ₃ ³⁾	1.26

¹⁾ Calculated from Weissenberg photographs.

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

³⁾ Calculated from powder photographs, 00 l row.

* Dimensions given correspond to 00 l and $hk0$ reflexions.

content of bismuth. Thus, for a sample with 81.8 % Bi_2O_3 the dimensions were $a = 3.88$ Å and $c = 14.78$ Å and for a sample with 80.6 % 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 00 l 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 00 l 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 $\text{R} \cdot \text{COO} \cdot \text{O} \cdot \text{Bi}$. A similar structural unit has previously been observed for bismuth oxide chloride BiOCl^2 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):	$0, \frac{1}{2}, z$; $\frac{1}{2}, 0, \bar{z}$	$z = 0.171$
2 Cl	at 2(c):	$0, \frac{1}{2}, z$; $\frac{1}{2}, 0, \bar{z}$	$z = 0.650$

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

Weissenberg photographs ($h0l$ and $h1l$) were taken of a crystal of the bismuth oxide formate using $\text{Cu-K}\alpha$ radiation. The Laue symmetry was found to

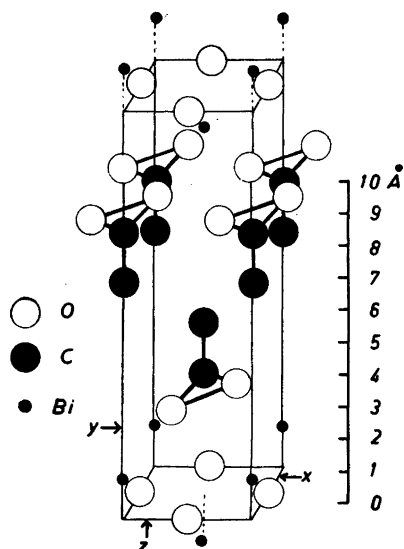


Fig. 1. Tentative structure of bismuth oxide acetate. The origin used in the figure corresponds to the point $\frac{1}{2}, 0, \frac{1}{2}$ in the monoclinic cell described in the text.

carboxyl groups is similar to the problem of the arrangement of the carbonate ions of the minerals bismuthite ($\text{Bi}_2\text{O}_2\text{CO}_3$) and beyerite ($\text{CaBi}_2\text{O}_2(\text{CO}_3)_2$), treated by Lagercrantz and Sillén⁵. 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. $\text{Bi}-\text{O}_{\text{carboxyl}} = 2.4 \text{ \AA}$ for the ordered alternative and $2.4-2.7 \text{ \AA}$ for the random one while $\text{C}-\text{C}$ (of the same layer) = 3.97 \AA and $\text{C}-\text{C}$ (of adjacent layers) = 3.6 \AA .

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 \AA^2 as compared with the value $18.2-18.9 \text{ \AA}^2$ obtained for potassium soaps (angle of tilt $53-55^\circ$) by Lomer⁶, the value 17.4 \AA^2 obtained by Vand, Aitken and Campbell⁷ for silver caproate at 20° C (angle of tilt 73°), both determined by X-ray methods, and the value 21 \AA^2 obtained from surface measurements by Langmuir⁸ 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 accommodate themselves easily to the restricted mesh of the Bi_2O_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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