The Crystal Structure of Antimony(III) Pyrogallate, $Sb(C_6H_3O_3).H_2O$

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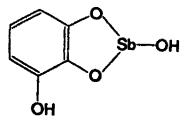
Pyrogallol, $C_6H_6O_3$, has been used as an analytical reagent for antimony and bismuth because colourless $Sb(C_6H_3O_3).H_2O$ and yellow $Bi(C_6H_3O_3)$ are only slightly soluble in water solution.[1] The reagent may be used for quantitative determination of Sb^{3+} and Bi^{3+} either alone or in presence of ions of Zn, As or Pb.[2] Geometrical considerations show that one Sb or Bi cannot be bonded to all three oxygen atoms of one pyrogallate ion. For the Sb compound the structural formula may be



with three-coordinated Sb as proposed by Feigl[1] or a structure with four-coordinated Sb bonded to two or more pyrogallate ions. The second alternative seems to be the most probable.

$Sb(C_6H_3O_3).H_2O$ and $Bi(C_6H_3O_3)$ were synthesized according to the method of Vogel.[2] The X-ray powder photographs were interpreted by orthorhombic unit cells. The diffractograms indicate that the Sb and Bi compounds are very similar in spite of their different water content. The following lattice parameters were obtained with the aid of least-squares calculations.

	$Sb(C_6H_3O_3).H_2O$	$Bi(C_6H_3O_3)$
a/Å	8.4168(12)	8.5515(11)
b/Å	15.982(3)	16.063(3)
c/Å	4.7871(9)	4.6799(7)
V/Å^3	643.9(2)	642.8(2)

Single crystal measurements were made for the antimony pyrogallate compound. Weissenberg photographs showed the following conditions limiting possible reflexions: hkl only with $k+l=2n$ and $h0l$ only with $h=2n$, which are characteristic for the space groups $Amam$ (No. 63), $Ama2$ (No. 40) and $A2_1am$ (No. 36). The observed density (by floation) is 2.62 g cm^{-3}, in good agreement with the calculated density of 2.71 g cm^{-3} for four formula units per unit cell. Thus the unit cell contains four Sb atoms. Because of the very low observed intensity of all reflexions with $h=2n+1$, the positions

Table 1. Final positional and thermal parameters for Sb(III) pyrogallate. Standard deviations are given within parentheses. The anisotropic thermal parameters are based on the expression $\exp[-(h^2\beta_{11}+k^2\beta_{22}+l^2\beta_{33}+2hk\beta_{12}+2hl\beta_{13}+2kl\beta_{23})]$.

Atom	x	y	z	B/Å^2	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Sb	0	0	0		.00459(7)	.00151(2)	.0156(3)	.0002(1)	0	0
O1	¼	.0309(6)	−.113(3)		.0037(10)	.0016(2)	.031(6)	0	0	.003(1)
O3	¼	.3946(8)	−.278(5)		.0114(16)	.0037(6)	.030(13)	0	0	.003(2)
O2	−.0298(7)	.0904(4)	−.291(2)		.0043(10)	.0020(2)	.040(6)	.0009(3)	.0008(13)	.0024(8)
C1	¼	.0934(8)	−.307(6)	1.48(23)						
C4	¼	.2179(8)	−.701(4)	1.81(21)						
C2	.1028(11)	.1238(5)	−.401(2)	1.47(12)						
C3	.1059(12)	.1868(5)	−.599(3)	1.82(14)						
H4	¼	.2643	−.845	2						
H3	.0118	.2087	−.670	2						

4(c) in *Amam*, 4(b) in *Ama*2 and 4(*a*) in $A2_1am$ did not seem probable for the Sb atoms. The positions 4(*a*) and 4(*b*) in *Amam* are not compatible with the presence of the stereochemically active lone pair of the Sb atoms, since their point symmetry is 2/*m*. Thus space group *Ama*2 was used and the four Sb atoms were assumed to occupy the position 4(*a*) with $z = 0$ whereby the origin of the unit cell was fixed.

A single crystal ($0.065 \times 0.014 \times 0.283$ mm^3) was mounted on a Pailred diffractometer along the crystallographic *c* axis (the 0.283 mm direction). Totally 1041 reflexions were collected using Mo$K\alpha$ radiation ($\lambda = 0.71069$ Å). The conditions for recording and reducing the intensities were mainly the same as described by Aurivillius and Malmros.[3] 417 intensities were considered unobserved, being weaker than 2.58 $\sigma(I)$, where $\sigma(I)$ is the standard deviation of the intensity based on counting statistics. 4 weak intensities were rejected because of uneven backgrounds. The remaining 620 intensities contained both *hkl* and $h\bar{k}l$ reflexions. After corrections for Lorentz, polarization and absorption effects ($\mu_{MoK\alpha} = 42.9$ cm^{-1}), the corresponding observed reflexions were average and 309 independent reflexions thus remained from the diffractometer measurements.

Having fixed the positions of the Sb atoms, the positions of the C and O atoms were found from difference Fourier maps. Least-squares refinements were made using anisotropic temperature factors for the Sb and O atoms and isotropic ones for the C atoms. The positions of the non-water hydrogen atoms were deduced from geometrical considerations and their temperature factors were fixed to agree with those of the corresponding carbon atoms. The parameters of the hydrogen atoms were not varied during the least-squares calculations. Anomalous dispersion was finally introduced for the Sb atoms and the weighted *R*-value was 0.0332. The signs of all *z* coordinates were reversed together with the signs of the terms β_{13} and β_{23} belonging to the anisotropic temperature factors. A new refinement gave the value 0.0327 for the weighted *R*-factor. Thus the structure of the single crystal used could best be described by the last-mentioned parameters. The final conventional *R*-factor is 0.023 for 309 reflexions. The antimony atoms do not contribute to 25 reflexions with $h = 2n + 1$. The separate *R*-factor for these reflexions is 0.066. Positional and thermal parameters are listed in Table 1. Lists of $|F_o|$ and $|F_c|$ are available on request.

The crystal structure of antimony pyrogallate is mainly as could be expected from the present knowledge of the coordination of antimony(III).[4] Each antimony atom is coordinated to four oxygen atoms belonging to two pyrogallate ions (*cf.* Fig. 1) in such a way that endless isolated chains of composition $Sb(C_6H_3O_3)$ parallel to the crystallographic *a* axis are formed. The Sb–O distances and

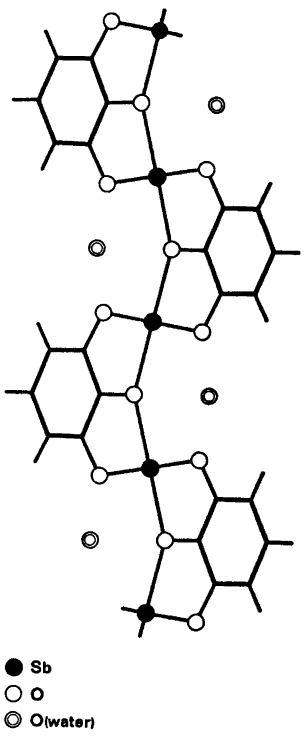


Fig. 1. A projection along the *c*-axis of an endless chain of composition $Sb(C_6H_3O_3).H_2O$. The chain is parallel to the *a*-axis. The water molecules are also indicated.

O–Sb–O angles agree well with the ones found for other four-coordinated Sb(III)-oxygen compounds. In addition to the four oxygen atoms at close distances, the Sb atom has two water molecules as next nearest neighbours at the distance 2.91(1) Å (*cf.* Fig. 1). Hydrogen bonds may be present between the water oxygen and the pyrogallate oxygens at the distance 2.71(2), 2.99(2) and 2.99(2) Å. Two antimony atoms, and one water oxygen atom

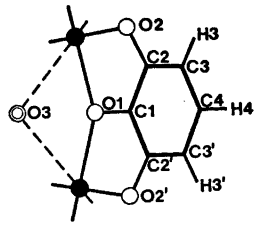


Fig. 2. A projection along the *c*-axis showing a part of the endless chain and a water molecule in order to illustrate the formation of the chelate rings.

Table 2. Distances (Å) and angles (°) in the SbO_4-polyhedron. The labeling of the atoms is given in Fig. 2.

	Present compound	$K_2[Sb_2(C_4H_2O_6)_2].3H_2O$[5]	$Fe(C_{12}H_8N_2)_3Sb_2(C_4H_2O_6)_2.8H_2O$[6]
Distances			
Sb–O2	2.022(9)	2.06(3), 2.01(3)	1.94(1)
Sb–O2′		2.05(2), 1.91(3)	1.94(1)
Sb–O1	2.228(4)	2.25(3), 2.22(3)	2.11(2)
Sb–O1′		2.17(3), 2.16(3)	2.16(2)
Angles			
O1–Sb–O1′	151.8(8)	147(1), 151(1)	153.5(7)
O1–Sb–O2	78.0(3)	77(1), 79(1)	79.7(6)
O1–Sb–O2′	82.7(4)	78(1), 80(1)	82.7(5)
O1′–Sb–O2	82.7(4)	82(1), 81(1)	84.9(5)
O1′–Sb–O2′	78.0(3)	79(1), 86(1)	79.1(5)
O2–Sb–O2′	92.9(9)	94(1), 103(1)	100.3(6)

are situated close to the plane formed by the corresponding pyrogallate ion (Fig. 2). The largest deviation from the best plane through the pyrogallate ring is 0.04 Å for the Sb atoms and 0.35 Å for the water oxygen atom. In this way three rings are formed which are nearly coplanar with the benzene ring, namely two five-membered chelate rings SbO_2C_2 and one four-membered ring containing two antimony atoms, one pyrogallate oxygen atom and one water oxygen atom. In Table 2 selected distances and angles of the present compound are compared to corresponding values for two other compounds where Sb also takes part in two five-membered chelate rings.

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