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MOLECULAR STRUCTURE OF ETHYLENEDIAMINE-N,N,N',N'-TETRAACETATO COMPLEX OF ANTIMONY(III): $HSb(C_{10}H_{12}N_2O_8)\cdot 2H_2O$

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The titled complex crystallizes in the monoclinic space group Pc with a=7.341, b=18.496, c=13.21 Å, β=123.8°, and Z=4. The structure of crystallographically different molecules in the unit cell are almost identical. Two N and four O atoms of the sexadentate ligand and a lone electron pair form a ψ-pentagonal bipyramid around the antimony atom.

The microcrystalline EDTA complex of antimony(III), $HSb(III)Y\cdot 2H_2O$ (H_4Y = ethylenediamine-N,N,N',N'-tetraacetic acid), was already obtained by Bhat and Iyer,[1] and its formation constant in aqueous medium was also reported.[1,2] In spite of its apparent high stability,[1] antimony(III) in its EDTA complex is easily and completely substituted by zinc(II), even though the formation constant of the latter is lower than that of the former. With regard to the method of investigation of aminopolycarboxylates of antimony, and other related elements of the main groups IV and V, the present authors have succeeded in determining the crystal and molecular structure of the titled complex by the X-ray method.

The complex $HSb(III)Y\cdot 2H_2O$ was prepared by the Bhat and Iyer's method,[1] and its single crystals were obtained by the recrystallization from the mixed solvent of acetonitrile and water (3:1 in v/v). The crystals obtained were brittle thin plates and stable in the open air. A 0.3× 0.3× 0.01 mm crystal was used for the measurements. The crystal data were: $C_{10}H_{17}N_2O_{10}Sb$, F.W.= 447.01, monoclinic, space group Pc, a=7.341±0.009, b=18.496±0.004, c=13.21±0.03 Å, β=123.8±0.1°; U=1489±3 Å^3, D_x=1.99, D_m=1.98±0.02 g cm^{-3}, Z=4. Intensity data were collected by ω-2θ scan technique (2θ<60°) on a Rigaku automated four circle diffractometer using Mo$K\alpha$ radiation (0.71073 Å). Of independent 4656 reflections 3423 non-zero ones were used for calculation. The positions of Sb atoms were deduced from a three-dimensional Patterson map, and the remaining non-hydrogen atoms were located in the subsequent Fourier maps. The structure has been refined by the block-diagonal least squares method to R=0.046 with anisotropic temperature factors. The projection of a molecule along the b-axis is shown in Figure 1. There have been observed no remarkable difference in their structures of two crystallographically independent molecules in the unit cell; the structure analysis in detail will be reported later on.

The average interatomic distances and bond angles of the both chelates in the same unit cell are as follows: Sb-N(1) 2.31±0.01, Sb-N(2) 2.39±0.01, Sb-O(1) 2.78±

0.02, Sb-O(2) 2.23±0.01, Sb-O(3) 2.18±0.02, Sb-O(4) 2.19±0.01 Å; N(1)-Sb-N(2) 76.4 ±0.4, N(1)-Sb-O(2) 71.6±0.5, N(2)-Sb-O(1) 64.8±0.5, O(1)-Sb-O(2) 149.5±0.6, O(3)-Sb -O(4) (axis) 142.7±0.5°. The atoms Sb, N(1), N(2), O(1), and O(2) are almost on a plane; the deviations of these atoms from the calculated best plane are within the range of 0.3 Å.

The distance between Sb and O(1) is a little longer than the other Sb-O ones, but all the oxygen atoms including O(1) are likely to be bonded with the central Sb atom. Since the positions of hydrogen atoms have not yet been revealed at the present stage of refinement, it can not be decided that the compound is an antimonic acid with H_3O^+ ion separated far from the carboxylato group, or is an acidic salt with one undissociated -COOH group. In aqueous solution, it was observed that this compound is of stronger acidity as compared with a common carboxylic acid.

The EDTA chelate of Sn(II), which is isoelectronic to Sb(III), has a ψ-pentagonal bipyramidal structure including a lone electron pair,[3] while the lone electron pair appears to be replaced by a water molecule in the pentagonal bipyramidal complex of the Sn(IV)-EDTA.[4]

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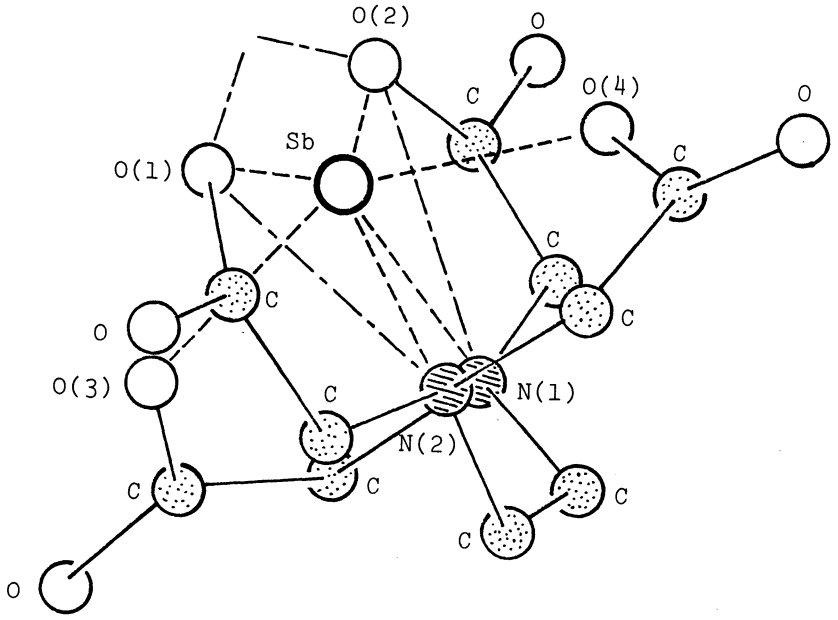

Fig.1. Molecular structure of Sb(III)Y moiety in HSb(III)Y·$2H_2O$
- ——— - ——— : planar ψ-pentagon, ------: coordination bond of the molecule.

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