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Figure 1

Figure 1: Figure 1

Abstract

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CRYSTAL STRUCTURE OF MIXED d,l-NH_4Sb-TARTRATE d,l-$(NH_4)_2[Sb_2(C_4H_4O_6)_2] \cdot 4H_2O$

Numerous works have been devoted to the structure of the complex formed by antimony with tartaric acid, and yet the question has not been finally resolved.

K, Rb, and NH_4 active and racemic Sb-tartrates were obtained in the laboratory of A. V. Ablov and kindly placed at our disposal for study. From the first X-ray results (^{1}) it followed that the least difficult objects for solving the crystal structure should be the isomorphous racemic d,l-RbSb-tartrate and d,l-NH_4Sb-tartrate.

According to (^{1}), single crystals of this isomorphous pair have the following parameters: ammonium
$a = 13.81 \pm 0.02, \quad b = 8.37 \pm 0.02, \quad c = 16.01 \pm 0.03$ Å,
$\beta = 94^\circ \pm 30'$, $Z = 8$, rubidium:
$a = 13.87 \pm 0.04, \quad b = 8.54 \pm 0.03,$

Fig. 1. Projection of the electron density $\sigma(x,z)$, calculated taking into account the contributions from all atoms. Crosses indicate the positions of atoms fixed from the three-dimensional distribution $\rho(x,y,z)$

$c = 15.73 \pm 0.03$ Å, $\quad \beta = 94^\circ \pm 30', \quad Z = 8$. The extinction of layer lines observed in the diffraction patterns corresponds to two space groups:
$C_s^4 = Cc$ and $C_{2h}^6 = C2/c$; both ensure a joint packing, in the same plane c, of the right and left isomers of the acid. Measurements at the Department of Crystal Physics of Moscow University showed either a complete absence of the piezoelectric effect in the NH_4-salt, or a very weak effect in the Rb-salt. The distribution of peaks on Patterson projections and the statistics of reflection intensities in the zones $0kl$ and $h0l$ for both crystals made it possible to begin the structure determination within the centrosymmetric group $C2/c$.

From the Patterson projections $P(x,z)$ and $P(y,z)$, constructed for both crystals, the coordinates of Sb and of the mutually substituting pair Rb—NH_4 were fixed. Projections of the electron density $\sigma(x,z)$ and $\sigma(y,z)$, taking into account

Fig. 2. Dimeric molecule of active tartaric acid

Figure 2: Fig. 2. Dimeric molecule of active tartaric acid

only the heavy atoms, as well as difference projections—with the Sb contribution removed—Fourier syntheses did not permit the light atoms to be localized unambiguously because of the overlap of two or more atoms (Fig. 1). To resolve them, were constructed

weighted projections of the electron density $S_1(x,z)$ and $C_1(x,z)$ according to signs determined by the contribution of Sb (for the NH_4-racemate). The roughly determined y-coordinates of the light atoms from the weighted projections were identified on the projections $\sigma(y,z)$, and as a result we had all three coordinates for 11 and 13 light atoms; the positions of 2 atoms remained indistinct. Next, ordinary and weighted projections of the electron density were constructed with allowance for all atoms, and difference projections after subtraction of the heavy atom. Refinement of the x and z coordinates for overlapping atoms was carried out by the method of phase projections (^{2}).

Fig. 2. Dimeric molecule of active tartaric acid according to (^{1}). Each half (HCOH—COOH) is flat; the angle between the planes of the halves (I and II) is 63°. The carbon atoms also lie approximately in one plane.

In constructing the structural model we proceeded from the configuration (Fig. 2) of the molecule that had earlier been established for crystalline active and racemic tartaric acid, and also for some of its NaK salts ($^{3-6}$). However, in the working model constructed, some interatomic distances remained unsatisfactory.

To refine and localize 2 doubtful atoms, a three-dimensional array of structural amplitudes of NH_4Sb-tartrate was created with the complete set of reflections $h0l$, $h5l$, $0kl$, $1kl$, and $hk0$—in all, ~ 1150 nonzero reflexions. At the Computing Center of the Institute of Chemical Physics of the Academy of Sciences of the USSR, after bringing all amplitudes to a common (absolute) scale and refining the coordinates of the heavy atom by the least-squares method, 16 sections of the three-dimensional electron-density distribution were computed. The discrepancy factor (without zero reflections and without contributions from two light atoms) was 24.0%.

Analysis of the three-dimensional distribution confirmed the correctness of the chosen structural model and gave the coordinates of all atoms. After their refinement by the least-squares method, with allowance for individual isotropic temperature corrections, the discrepancy factor decreased to 15.14%. Table 1 gives the final atomic coordinates, and Fig. 3 shows the xz projection of the structure of racemic NH_4Sb-tartrate.

Two residues of tartaric acid (of one optical sign), together with two Sb atoms, form an "island" around a 2-fold rotation axis. Each Sb atom is bonded to atoms O_4 (from the hydroxyl group) and O_6 (from the carboxyl group) of the

Fig. 3. Projection of the structure of d,l-ammonium antimonotartrate onto the (x,z) plane.

Figure 3: Fig. 3. Projection of the structure of d,l-ammonium antimonotartrate onto the (x,z) plane.

"upper" half of one molecule (residue), and to two atoms of the "lower" half of another residue, O_1' and O_3', with distances: (Sb—O_4) = 2.04, (Sb—O_6) = 2.14, (Sb—O_1') = 2.16, and (Sb—O_3') = 2.04 Å. These four O atoms nearest to Sb from two residues form a distorted and flattened tetrahedron; however, Sb itself lies outside the tetrahedron, and on the "other" side of Sb there are no neighboring atoms that could complete the coordination polyhedron. The molecule $(H_2O)_1$ and atom O_2 from a neighboring island are at distances of 3.40 and 2.99 Å, respectively, from Sb.

In accordance with the theory developed as early as 1940 by Sidgwick and Powell (7), one may expect that in trivalent antimony the lone pair of electrons occupies a definite position in the coordination sphere. This is very clearly—according to Biström (8)—manifested in the rhombic (valentinite) and cubic (senarmontite) modifications of antimony oxide Sb_2O_3, in the structures of which the Sb atoms have three O atoms at distances of 2.0-2.1 Å—and all "on one side."The geometry of the structure supports the assumption of such localization of the "sterically active" pair of lone 4th and 5th electrons of the Sb atom, which brings the coordination of Sb to tetrahedral. Although coordination 3 (+1) appears quite natural for Sb, nevertheless in recent years in a number of Sb compounds (9,10) a coordination 4 (+1) has been established, from four ligands at the vertices of a distorted tetrahedron (or square) plus—on the other side—the "sterically active" un-

Table 1

Coordinates of the atoms of d,l-NH_4Sb-tartrate

Atom	x/a	y/b	z/c	Atom	x/a	y/b	z/c
Sb	0.125	0.332	0.136	$(H_2O)_I$	0.179	0.002	0.019
O_1	0.155	0.120	0.211	$(H_2O)_{II}$	0.123	0.763	0.244
O_2	0.314	0.537	0.158	C_1	0.335	0.647	0.201
O_3	0.382	0.923	0.247	C_2	0.347	0.812	0.180
O_4	0.492	0.725	0.124	C_3	0.407	0.828	0.109
O_5	0.375	0.103	0.075	C_4	0.442	−0.003	0.091
O_6	0.033	0.532	0.104	NH_4	0.023	0.892	0.098

Fig. 3. Projection of the structure of d,l-ammonium antimonotartrate onto the (x,z) plane. Intramolecular bonds are shown by solid lines; hydrogen bonds formed by the molecule $(H_2O)_I$ with the O atoms of the residues are shown

by dashed lines; dotted lines indicate the bonds formed by Sb, and one of the bonds formed by NH_4.

a separated pair of electrons. The coordination in our mixed tartrate is the same. As indicated, the square (flattened tetrahedron) of 4 ligands is strongly distorted and, taking into account the 5th electron ligand, it is already difficult to speak of a coordination tetragonal pyramid; instead, a satisfactorily expressed trigonal bipyramid appears.

During the determination of the structure of the Rb- and NH_4Sb racemates, a communication was received that D. Grdenić and B. Kamenar (^{11}) had determined the structure of a racemic KSb tartrate analogous in composition but, as we established earlier (^{1}), nonisomorphous with the Rb–NH_4 pair. The authors state that in this compound the "ligands" around antimony are three O atoms from the tartrate residue and one O atom from a water molecule, and they also consider that an unshared pair of electrons completes the coordination polyhedron to a distorted trigonal bipyramid. Differences are noted in the manner in which Sb is attached to the acid residue, but unfortunately the available data are only the theses of the authors' report at the Rome (1963) crystallographic congress.

The islands (rings) described are essential elements of the structure. The acid residues are linked into a dimer through Sb atoms, and also through those O atoms whose mutual distances are smaller than intermolecular contacts: O_3^I—O_6 = (2.75 Å) and O_4—O_1^I = 2.71 Å. The islands along the twofold axis, i.e., in the direction of the shortest translation b (8.37 Å), form columns, which are cemented by $(H_2O)_{II}$ molecules forming hydrogen bonds $(H_2O)_{II}$—O_3 = 3.02 Å and $(H_2O)_{II}$—O_1 = 3.01 Å. The islands are also united into columns by coordination polyhedra around NH_4, in the formation of which the atoms O_6, O_2, and both H_2O molecules participate. In the plane parallel to (xy), the islands form a centered lattice with pseudohexagonality ($a : b \simeq \sqrt{3}$), clearly expressed on the Laue photograph taken along the c axis of the crystal. Islands from different columns are connected into this network by a system of hydrogen bonds created by the $(H_2O)_I$ molecule with O atoms from the tartrate residues.

Infinite nets parallel to (xy) alternate along the z axis with analogous nets composed of dimers of the opposite optical sign and related to the first by inversion centers. In the mutual interlacing of nets of the two kinds, the main role is played by hydrogen bonds: O_5—$(H_2O)_I$ = 2.95 Å and O_2—$(H_2O)_I$ = 2.842 Å.

Thus, in crystalline NH_4 antimonotartrate the principal cores should be considered to be dimeric complexes $[Sb_2(C_4H_4O_6)_2]^{2-}$, packed into columns (parallel to the b axis), and further into a three-dimensional framework by means of a system of hydrogen bonds. Four water molecules participate in the formation of the latter. Apparently, the H_2O molecule that entered into the composition of the complex whose structure was determined by chemical methods here loses the significance of a "coordination unit" and plays the role of water of crystallization. Racemic NH_4- and Rb-antimonotartrates in the crystalline state can then be represented as $A_2[Sb_2(C_4H_4O_6)_2] \cdot 4H_2O$, where $A = Rb, NH_4$. In the structure, and therefore also in the formula, there is no antimonyl group SbO; and it should be noted that, contrary to chemistry courses even of the late 1950s, in the new edition of Remy' s textbook (^{17}) we likewise do not find an SbO group in the formula of emetic tartar.

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