CRYSTAL STRUCTURE OF AMMONIUM BIS-μ-(d-TARTRATO)DISTIBATE (III)\

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Abstract

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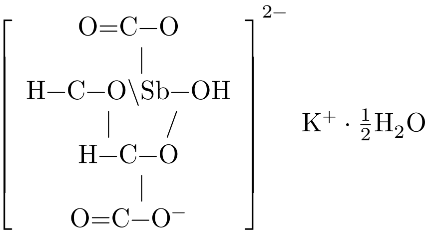
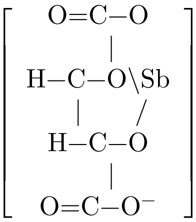
CRYSTAL STRUCTURE OF AMMONIUM BIS-μ-(d-TARTRATO)DISTIBATE (III)*

Until recently, for tartar emetic d-$KSbC_4H_2O_6 \cdot 1\frac{1}{2}H_2O$, the most substantiated structural formula was considered to be formula I (2). It satisfactorily explained why mesotartaric acid, in contrast to optically active isomers and their racemate, does not give a compound analogous to tartar emetic. In formula I, one coordination position around the Sb atom is occupied by an H_2O molecule. However, Spacu and Pîrtea (3) obtained salts $[M(NH_3)_6]^{3+}[SbC_4H_2O_6]_2NO_3$ (where $M = Co, Cr$), in which for each Sb there is one molecule of water less than in formula I, and they propose formula II for the tartrato-stibate ion. According to Girard and Lecomte (4), likewise, H_2O in tartar emetic is not coordinated with Sb. Bollard, on the basis of IR spectra, proposed for tartar emetic a structure with an Sb atom in a distorted trigonal bipyramid; in its poles are located the O atoms of two carboxyl groups, in two equatorial vertices–OH groups from tartrate ions, while the third equatorial vertex is unoccupied (5).

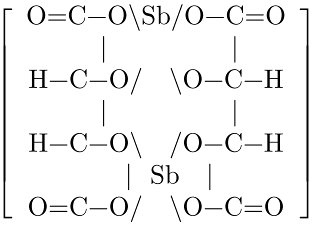
In the formulas presented, the tartar-emetic complex is tacitly assumed to be mononuclear. Cryoscopic measurements long ago led Kahlenberg to propose a doubled formula for tartar emetic (6), but such a formula was usually rejected on the grounds that the results (6) were obtained with comparatively concentrated solutions, where association, etc., is possible (2,7).



I



II



III

Only X-ray structural analysis can resolve the increasingly complicated questions of the structure of tartar emetic. At its first stage, analogues of tartar emetic with *dl*-tartaric acid proved convenient for study. The determination of the structures of isomorphous racemic salts $dl\text{-MSbC}_4\text{H}_2\text{O}_6 \cdot 2\text{H}_2\text{O}$ (M = Rb^+ or $\text{NH}_4{}^+$) showed that the complex anion $[\text{Sb}_2(d\text{-C}_4\text{H}_2\text{O}_6)_2]^{2-}$ is indeed a dimer (formula III) (^{8}), which contains on two Sb(III) two *d*- or two *l*-tartrate ions.

However, Gredenich and Kamenar (^{9,10}), studying the K salt of the racemate $dl\text{-KSbC}_4\text{H}_4\text{O}_7 \cdot \frac{1}{2}\text{H}_2\text{O}$, nevertheless speak of a mononuclear complex corresponding to Reihlen' s formula. This discrepancy of results, difficult to explain by the different sizes of K^+ in (^{9,10}) and Rb^+ or $\text{NH}_4{}^+$ in (^{8}), compelled us to investigate optically active antimony-tartrate complexes of the tartar-emetic type, namely the isostructural series $\text{M}_2[\text{Sb}_2(d\text{-T})_2] \cdot 3\text{H}_2\text{O}$,

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* A preliminary communication was made at the VII International Congress of the Union of Crystallographers, Moscow, 1966 (^{1}).

where (d-T) is the d-tartrate ion $(\text{C}_4\text{H}_2\text{O}_6)^{4-}$, and $M = \text{K}^+$, Rb^+, or $(\text{NH}_4)^+$, crystallizing in the orthorhombic group $C222_1$ with parameters:

$$M = \text{K}^+, \quad a = 11.23 \pm 0.03, \quad b = 11.72 \pm 0.03, \quad c = 26.01 \pm 0.07\ \text{Å}; \quad (1)$$

$$M = \text{Rb}^+, \quad a = 11.37 \pm 0.03, \quad b = 12.13 \pm 0.03, \quad c = 26.10 \pm 0.07\ \text{Å}; \quad (2)$$

$$M = (\text{NH}_4)^+, \quad a = 11.10 \pm 0.03, \quad b = 12.32 \pm 0.03, \quad c = 26.35 \pm 0.07\ \text{Å}. \quad (3)$$

$Z = 8$ formula units of the indicated compositions $^{(11)}$. Crystals of the K salt rapidly weather in air, and three-dimensional sets of intensities (equi-inclination X-ray goniometer, Cu $K\alpha$, $(\sin\theta/\lambda)_{\max} \simeq 0.6$ Å, multiple exposures) were obtained from crystals of the Rb and NH_4 compounds. For the former, from the reciprocal-lattice layers $h0l$, $h1l$, $0kl \rightarrow 4kl$, $hk0$, about 600 independent nonzero reflections were obtained; for the latter, about 850 ($h0l \rightarrow h5l$, $0kl$, $hk0$, hhl). Intensities were estimated on a $4\sqrt{2}$ blackening scale and corrected for the (LP) factor without allowance for absorption.

The positions of the Sb atoms and of the isomorphously substituting Rb^+ and NH_4^+ were found from comparison of three-dimensional Patterson functions calculated independently for the Rb and NH_4 salts.

Table 1

Atomic coordinates

Atom	x/a	y/b	z/c	Atom	x/a	y/b	z/c
Sb_1	0.386	0.161	0.049	O_{H_2O} (I)	0.442	0.522	0.143
Sb_2	0.128	0.318	0.193	O_{H_2O} (II)	0.324	0.795	0.046
O_1	0.198	0.097	0.031	O_{H_2O} (III)	0.317	0.759	0.184
O_2	0.034	0.166	0.010	C_1	0.135	0.184	0.041
O_3	0.299	0.296	0.060	C_2	0.173	0.295	0.035
O_4	0.071	0.292	0.120	C_3	0.101	0.368	0.085
O_5	0.170	0.532	0.071	C_4	0.158	0.463	0.096
O_6	0.198	0.461	0.148	C_5	0.234	0.030	0.208
O_7	0.143	0.161	0.203	C_6	0.325	0.174	0.193
O_8	0.243	0.003	0.229	C_7	0.430	0.100	0.167
O_9	0.311	0.289	0.200	C_8	0.001	0.711	0.143
O_{10}	0.333	0.059	0.114	N_1	0.110	0.940	0.101
O_{11}	0.078	0.753	0.172	N_2	0.000	0.957	0.250
O_{12}	0.008	0.747	0.096	N_3	0.407	0.500	0.000

for the Rb and NH_4 salts. Neither centrosymmetric projections $\sigma(x, z)$, $\sigma(y, z)$, nor three-dimensional Fourier syntheses constructed from the coordinates of the heavy atoms alone made it possible to localize unambiguously the light atoms of the structure.

The [110] projection of the electron density along the shortest translation in the cell proved to be exceptionally "effective." The second-order axes parallel to the centered (C) face are oblique to [110] and disappear in projection; that is, the number of "independent" atoms is thereby doubled, and the structure is visible in two "views," which makes it possible to determine all three coordinates of each atom from a single map. The projection $\sigma(x', z)$, taking account only of Sb atoms, was constructed for the NH_4 salt and revealed the positions of the tartrate ions and H_2O molecules. (Subsequently, all calculations were carried out only for this compound.) The atomic coordinates were refined from three-dimensional distributions. Two cycles including all atoms except H gave $R =$ 33.4 and 29.6%. Refinement by the least-squares method reduced R to 20.4%. (Table 1 gives the coordinates obtained in the last refinement cycle. The overall isotropic temperature factor is $B = 3.66\ \text{Å}^2$.)

As in racemic NH_4–Sb tartrate (8), two Sb atoms and two d-tartrate ions form a binuclear complex anion $[Sb_2(d\text{-}T)_2]^{2-}$, the d-tartrate ions serving as bridges (Fig. 1). The rational name of the complex is bis-μ-(d-tartrato)distibate(III) ion. Around the Sb(III) atoms, two O atoms from hydroxyl groups are coordinated (mean $Sb - O_{hydr} = 2.02$ Å) and two O atoms from carboxyl groups (mean $Sb - O_{carb} =$

Figure 1

Figure 1: Figure 1

= 2.18 Å), belonging to two halves of two different *d*-tartrate ions in the trans position. A similar binuclear complex anion has been established in the structure $[Sb_2(d\text{-}T)_2][Fe^{II}phen_3] \cdot 8H_2O$ (^{13}).

All atoms of the binuclear complex occupy crystallographically independent positions and only slightly distort the intrinsic point symmetry of the complex $D_2 = 222$. The coordination polyhedron of Sb(III) is a distorted trigonal bipyramid, one of whose equatorial vertices is occupied by the lone pair of $5s^2$ electrons ("diagonal" angles: $O_{carb} - Sb - O_{carb} \simeq 150°$; $O_{hydr} - Sb - O_{hydr} \simeq 105°$). The form of the distorted "seesaw" is characteristic of most oxygen compounds of Sb(III) (^{12}). Retention of the $5s^2$ lone pair leads to the same configuration even in such oxygen-containing compounds of Sb(III) where the ligands are not isolated O atoms but polydentate groups forming chelates, and where, therefore, a strong distortion of the coordination polyhedron might be expected because of steric hindrance. An analogous environment of Sb is also found in the recently determined structure of H-bis(thioglycolato)stibate(III) (^{14}), where two thioglycolate ions form, with Sb(III), two five-membered rings, with the difference that two equatorial vertices are occupied by S atoms. We note that, because of steric hindrance, formation of binuclear complexes of μ-(d-tartrato)(l-tartrato)distibate(III) and bis-μ-(mesotartrato)distibate(III) is impossible, since complexes with meso-isomers would have the form of polymeric chains (Fig. 2)*. This is probably the main reason for the failures in isolating a crystalline product with mesotartaric acid (^{2}).

Fig. 1. Dimeric complex cation $[Sb_2(d\text{-}C_4H_2O_6)_2]^{2-}$.
$O_1 - Sb_1,\ O_{12} - Sb_1,\ O_6 - Sb_2,\ O_7 - Sb_2 \sim 2.18$ Å;
$O_3 - Sb_1,\ O_{10} - Sb_1,\ O_4 - Sb_2,\ O_9 - Sb_2 \sim 2.02$ Å;
$O_1 - Sb_1 - O_{12},\ O_6 - Sb_2 - O_7 \sim 150°$;
$O_3 - Sb_1 - O_{10},\ O_4 - Sb_2 - O_9 \sim 105°$.

In the structure of NH_4-bis-μ-(d-tartrato)distibate(III) one can distinguish infinite plane layers perpendicular to the z axis; in them the axes $2^{(3)}$ of the complexes (Fig. 1) are parallel to one another (Fig. 3). The thickness of each layer is $c/4$, and they are located between families of glide planes parallel to x and y, respectively. In neighboring layers the axes of the complexes intersect at an angle of $\sim 90°$. In each layer the complexes are arranged in a pseudosquare "network" $\left(\frac{1}{2}\sqrt{a^2 + b^2} \simeq (a+b)/\sqrt{2}\right)$, in accordance with the distorted tetragonal symmetry of the whole (group $D_4^3 = P4_122$). It may be noted that in the racemic compound (^{8}) layers of dimers of one optical sign are also distinguished; neighboring layers are constructed from signs—

Fig. 2. Probable form of chain complexes of antimony(III) with mesotartaric acid

Figure 2

Figure 2: Figure 2

Fig. 3. Projection of the structure along the diagonal of the centered face [110]

Figure 3: Fig. 3. Projection of the structure along the diagonal of the centered face [110]

* The complex in Fig. 2 was constructed on the basis of a model of the meso-tartaric acid molecule according to (^{15}).

thiomeric tartrate ions. In contrast to the *d*-compound, in the racemate the dimers are arranged in layers according to a pseudohexagonal planar net.

The 24 molecules of H_2O in three general positions participate in the coordination of the NH_4^+ ions and create a network of hydrogen bonds involving O atoms from the tartrate ions. The 16 NH_4^+ cations are located in two special positions (on twofold axes parallel to x and y) and in one general position. The coordination–

Fig. 3. Projection of the structure along the diagonal of the centered face [110]

polyhedra of the outer-sphere cations form infinite helical chains parallel to the z axis, "stitching together" the pseudosquare nets of the complexes. Together with the network of hydrogen bonds they link the structure into a three-dimensional framework.

The dimeric complexes $[Sb_2(dT)_2]^{2-}$ are sufficiently stable in aqueous solutions, as was shown earlier by the work of Kahlenberg (6).

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REFERENCES

1. G. A. Kiosse, N. I. Golovastikov, Abstracts of reports at the VII International Congress of Crystallographers, Moscow, July 1966, "Nauka," 1966, p. A–132.

2. H. Reihlen, E. Hezel, Lieb. Ann., 487, 213 (1931).
3. G. Spacu, D. Pirtea, Bull. Sect. Sci. Acad. Roumaine, 27, 138 (1944).
4. M. Girard, J. Lecomte, J. Phys. Rad., 17, 9 (1956).
5. J. Bolard, J. chim. phys., 62, 908 (1965).
6. L. Kahlenberg, Zs. phys. Chem., 17, 577 (1895).
7. M. Girard, Bull. Soc. chim. France, 1955, 571.
8. G. A. Kiosse, N. I. Golovastikov, N. V. Belov, DAN, 155, 545 (1964).
9. D. Grdenić, B. Kamenar, VI Intern. Congr. of Crystallography and Symosia, Rome, Italy, Abstr., Sect. 4, Abstr. 68, Sept. 1963.
10. D. Grdenić, B. Kamenar, Acta crystallogr., 19, 197 (1965).
11. G. A. Kiosse, N. I. Golovastikov, N. V. Belov, Crystallography, 9, 402 (1964).
12. T. N. Polynova, M. A. Porai-Koshits, ZhSKh, 7, 146 (1966).
13. D. H. Templeton, A. Zalkin, T. Ueki, Acta crystallogr., 21, 7, A-154 (1966).
14. I. Hansson, Chem. Commun., 4, 173 (1967).
15. G. A. Bootsma, J. C. Schoone, Acta crystallogr., 22, 522 (1967).

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