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Structure of Fluoro(1,10-phenanthroline)pyrocatecholatoantimony(III)

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Abstract. $C_{18}H_{12}FN_2O_2Sb$, M_r = 429·1, monoclinic, $P2_1/c$, a = 7·496 (2), b = 18·885 (2), c = 11·681 (1) Å, β = 99·70 (1)°, U = 1630 Å^3; Z = 4, D_c = 1·749 Mg m^{-3}, $F(000)$ = 840, Mo $K\alpha$ radiation, λ = 0·71069 Å, μ(Mo $K\alpha$) = 1·86 mm^{-1}. Final R = 0·051 for 2137 unique X-ray diffractometer data. The Sb atom is situated in a distorted square-pyramidal (ψ-octahedral) environment, with Sb—F 1·965 (7), Sb—O 2·063 (7)/2·007 (8), and Sb—N 2·569 (9)/ 2·448 (8) Å.

Introduction. This report is part of a structural study of antimony(III) compounds with oligodentate ligands. Only few structures of such compounds have been determined by diffraction methods and therefore information on effects of chelating ligands on the coordination geometry of Sb^{III} is scarce. In 'tartar emetic', $K_2Sb_2(C_4H_2O_6)_2.3H_2O$, Sb attains tetracoordination, the O atoms about Sb occupying four corners of a slightly distorted square pyramid, whose apex belongs to the unshared electron pair (Kamenar, Grdenić & Prout, 1970; Gress & Jacobson, 1974). In pyrogallolatoantimony(III), $Sb(C_6H_3O_3).H_2O$, a similar structure with four coordinating O atoms has been described (Aurivillius & Särnstrand, 1976). Chloropyrocatecholatoantimony(III), $C_6H_4O_2SbCl$, according to a partial structure determination, has a choro-bridged structure, Sb being coordinated by two O and two Cl atoms (Barnard, Donaldson & Tricker, 1979), while in methoxopyrocatecholatoantimony(III), $C_6H_4O_2SbOCH_3$, a distorted square pyramid of five O atoms about Sb has been found (Burschka, 1978), leaving space for an unshared electron pair below the base of the pyramid. Now it seemed worthwhile to elucidate the molecular structure of the present compound, it being the first example of an Sb complex with oligodentate ligands of which one is a neutral bidentate N donor. Interest also arose from the presence of fluoride in such a compound and the question of its structural function. The yellow compound has been prepared from $C_6H_4O_2SbF$ (Brown & Austin, 1941) with 1,10-phenanthroline in methanol, and was recrystallized from the same solvent (m.p. 546–548 K).

Data were collected with a crystal 0·20 × 0·13 × 0·17 mm. Lattice parameters were obtained by least squares from the diffractometer angles of 24 reflexions measured with a Nonius CAD-4 diffractometer with graphite-monochromated Mo $K\alpha$ radiation. The intensities of 2863 reflexions with $2 \leq \theta \leq 24°$ were measured by the $\omega/2\theta$ scan technique with a scan speed between 0·014 and 0·055° s^{-1} in 2θ. After averaging, 2137 observed reflexions [$I > 2\sigma(I)$] remained. The intensities were corrected for Lorentz and polarization effects but not for absorption.

Table 1. *Fractional atomic coordinates* (×10^4) *and U values* (Å^2 ×10^4) *with e.s.d.'s in parentheses*

	x	y	z	U
Sb(1)	179 (1)	61953 (4)*	−2208 (1)	343 (3)
F(1)	554 (10)	7192 (4)	−2587 (6)	541 (47)
O(1)	−125 (10)	6408 (5)	−519 (6)	492 (53)
O(2)	−2485 (9)	6399 (4)	−2433 (6)	364 (44)
N(1)	−1269 (12)	4976 (5)	−2697 (7)	350 (54)
N(2)	−962 (12)	6026 (5)	−4279 (7)	349 (54)
C(1)	−1831 (15)	6624 (6)	−431 (9)	380 (68)
C(2)	−2342 (18)	6843 (7)	605 (9)	469 (77)
C(3)	−4139 (17)	7036 (7)	603 (10)	443 (76)
C(4)	−5398 (16)	7015 (6)	−398 (10)	416 (73)
C(5)	−4865 (15)	6808 (6)	−1443 (10)	381 (69)
C(6)	−3099 (14)	6610 (5)	−1461 (8)	294 (59)
C(7)	−1376 (16)	4476 (7)	−1921 (10)	452 (76)
C(8)	−2264 (17)	3829 (7)	−2212 (11)	508 (80)
C(9)	−3056 (17)	3714 (7)	−3344 (12)	496 (81)
C(10)	−2945 (15)	4236 (6)	−4185 (10)	375 (67)
C(11)	−2033 (13)	4866 (5)	−3815 (9)	300 (59)
C(12)	−3754 (16)	4153 (7)	−5392 (11)	501 (80)
C(13)	−3605 (15)	4677 (7)	−6182 (10)	436 (72)
C(14)	−2657 (14)	5314 (6)	−5831 (9)	356 (64)
C(15)	−1858 (13)	5419 (5)	−4650 (8)	279 (57)
C(16)	−2496 (16)	5870 (7)	−6605 (10)	460 (75)
C(17)	−1570 (17)	6488 (7)	−6221 (9)	450 (74)
C(18)	−820 (15)	6549 (6)	−5031 (9)	386 (68)

* Multiplied by 10^5.

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The phase problem was solved from the Patterson function. The final refinement converged with anisotropic temperature factors for all non-H atoms and 217 refined parameters to an unweighted $R = 0{\cdot}05$.* H atoms were placed in geometrically calculated positions (C—H 1·09 Å, H—C—C 120°) after the last refinement cycle. A final difference map did not show significant peaks.

The final atomic positional parameters are listed in Table 1 together with equivalent temperature factors $U = \frac{1}{3}(U_{11} + U_{22} + U_{33} + 2U_{13}\cos\beta)$ for the non-H atoms.

The calculations were performed with the *Enraf–Nonius Structure Determination Package.* Complex neutral-atom scattering factors were taken from Cromer & Waber (1974) and Cromer (1974). The figures were drawn with *ORTEP* (Johnson, 1976) and *POP*1 written by van de Waal (1976).

Discussion. The molecule (with atomic numbering) is shown in Fig. 1 and a stereoview of the molecule is given in Fig. 2. The coordination about Sb is a distorted tetragonal pyramid with the atoms N(1), N(2), F(1) and O(1) forming the basis, O(2) being in the apical position. Ample space is left *trans* to O(2) and one can assume that the nonbonding electron pair is stereochemically active and is located in this gap, completing the coordination polyhedron about Sb to a distorted ψ octahedron.

Bond distances and angles are given in Table 2. It is remarkable that Sb(1)—O(2) [2·007 (8) Å], the bond *trans* to the assumed site of the lone pair, is significantly shorter than Sb(1)—O(1) [2·063 (8) Å]. Corresponding distances have been found in $C_6H_4O_2SbOCH_3$ for the three Sb—O bonds of the molecular unit [distances to the additional coordinated O atoms: 2·36 (1) and 2·65 (1) Å] (Burschka, 1978), and also a short bond between Sb and O forming the apex of the tetragonal pyramid has been observed.

The Sb—F distance of 1·965 (7) Å is in the upper range observed in compounds with 'terminal' fluoro ligands, *e.g.* in $Sb_2F_4Cl_5$: 1·88–1·94 Å (Müller, 1978), in $CsSb_2F_7$: 1·94–1·98 Å (Ryan, Mastin & Larson, 1971), in $SbF_3.2CH_3OC_6H_4NO.H_2O$: 1·91–1·97 Å (Dewan, Edwards, Guerchais & Petillon, 1975). Sb—F distances observed for Sb—F—Sb bridges (Ryan *et al.*, 1971; Müller, 1978) are significantly longer. The Sb—N distances of 2·448 (8) and 2·569 (9) Å are appreciably

Table 2. *Bond distances* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

Sb(1)—F(1)	1·965 (7)	C(8)—C(9)	1·37 (2)
Sb(1)—O(1)	2·063 (7)	C(9)—C(10)	1·40 (2)
Sb(1)—O(2)	2·007 (8)	C(10)—C(11)	1·40 (2)
Sb(1)—N(1)	2·569 (9)	C(11)—N(1)	1·35 (1)
Sb(1)—N(2)	2·448 (8)	C(10)—C(12)	1·45 (2)
O(1)—C(1)	1·36 (2)	C(12)—C(13)	1·37 (2)
O(2)—C(6)	1·35 (1)	C(13)—C(14)	1·42 (2)
C(1)—C(2)	1·39 (2)	C(14)—C(15)	1·42 (1)
C(2)—C(3)	1·40 (2)	C(15)—C(11)	1·45 (1)
C(3)—C(4)	1·37 (2)	C(14)—C(16)	1·40 (2)
C(4)—C(5)	1·40 (2)	C(16)—C(17)	1·39 (2)
C(5)—C(6)	1·38 (2)	C(17)—C(18)	1·41 (2)
C(6)—C(1)	1·40 (2)	C(18)—N(2)	1·34 (1)
N(1)—C(7)	1·32 (2)	N(2)—C(15)	1·36 (1)
C(7)—C(8)	1·40 (2)		

F(1)—Sb(1)—O(1)	94·1 (3)	C(1)—C(2)—C(3)	119 (1)
F(1)—Sb(1)—O(2)	87·9 (3)	C(2)—C(3)—C(4)	121 (1)
F(1)—Sb(1)—N(1)	151·6 (3)	C(3)—C(4)—C(5)	120 (1)
F(1)—Sb(1)—N(2)	86·7 (3)	C(4)—C(5)—C(6)	120 (1)
O(1)—Sb(1)—O(2)	79·6 (3)	C(5)—C(6)—C(1)	120 (1)
O(1)—Sb(1)—N(1)	106·1 (3)	C(6)—C(1)—C(2)	120 (1)
O(1)—Sb(1)—N(2)	153·4 (3)	C(11)—C(15)—N(2)	119 (1)
O(2)—Sb(1)—N(1)	76·7 (3)	N(1)—C(7)—C(8)	122 (1)
O(2)—Sb(1)—N(2)	73·8 (3)	C(7)—C(8)—C(9)	119 (1)
N(1)—Sb(1)—N(2)	66·3 (3)	C(8)—C(9)—C(10)	120 (1)
Sb(1)—O(1)—C(1)	112·7 (6)	C(9)—C(10)—C(11)	118 (1)
Sb(1)—N(1)—C(7)	124·1 (7)	C(10)—C(11)—N(1)	122 (1)
Sb(1)—N(1)—C(11)	116·6 (7)	C(11)—N(1)—C(7)	119 (1)
Sb(1)—N(2)—C(18)	119·9 (7)	C(11)—C(10)—C(12)	120 (1)
C(6)—O(2)—Sb(1)	114·7 (6)	C(10)—C(12)—C(13)	121 (1)
C(15)—N(2)—Sb(1)	119·7 (6)	C(12)—C(13)—C(14)	121 (1)
O(1)—C(1)—C(6)	116 (1)	C(13)—C(14)—C(15)	120 (1)
C(1)—C(6)—O(2)	117 (1)	C(14)—C(15)—C(11)	119 (1)
C(15)—C(11)—C(10)	120 (1)	O(2)—C(6)—C(5)	124 (1)
C(15)—C(14)—C(16)	117 (1)	N(1)—C(11)—C(15)	118 (1)
C(14)—C(16)—C(17)	121 (1)	C(18)—N(2)—C(15)	120 (1)
C(16)—C(17)—C(18)	119 (1)	N(2)—C(15)—C(14)	122 (1)
C(17)—C(18)—N(2)	122 (1)	C(9)—C(10)—C(12)	123 (1)
O(1)—C(1)—C(2)	124 (1)	C(13)—C(14)—C(16)	123 (1)

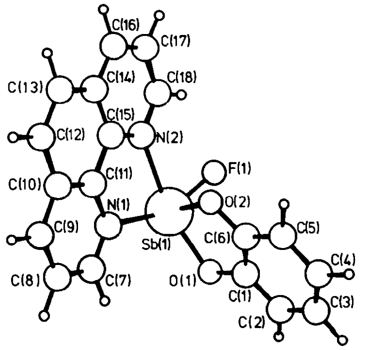

Fig. 1. A molecule of $C_6H_4O_2SbF.1,10$-phenanthroline showing the atom numbering. Numbers of H atoms (omitted for clarity) correspond to numbers of the C atoms to which they are bound.

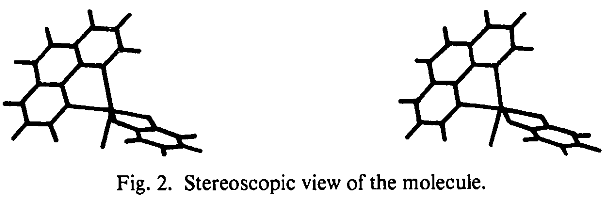

Fig. 2. Stereoscopic view of the molecule.

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* Lists of structure factors, thermal parameters and calculated H positions have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36424 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

longer than the sum of the covalent radii of 2·15 Å (Pauling, 1960), yet distinctly smaller than the sum of the van der Waals radii of 3·7 Å (Pauling, 1960). No structural information for other Sb^{III} complexes with neutral N-donor ligands is available. However, it is noteworthy that in the EDTA complex $HSb(C_{10}H_{12}N_2O_8).2H_2O$ the Sb—N distances [2·31 (1), 2·39 (1) Å] are also rather long (Kita, Uehiro, Iwamoto, Ouchi & Yoshino, 1976).

Intermolecular distances do not indicate interactions exceeding van der Waals forces.

The two least-squares planes defined by the atoms (I): C(*n*) (*n* = 1–6) and (II): N(1), N(2), C(*m*) (*m* = 7–18) show that the atoms in planes (I) and (II) respectively do not deviate significantly from them. The positions of the atoms Sb(1), O(1) and O(2) lie 0·097 (1), 0·039 (9) and 0·006 (7) Å respectively out of the plane (I), and Sb(1) lies 0·158 (1) Å out of plane (II). The angle between plane (I) and plane (II) is 96·6°.

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Structure of Manganese(II) L-Lactate Dihydrate

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Abstract. $Mn(C_3H_5O_3)_2.2H_2O$, orthorhombic, $P2_12_12_1$, $a = 6\cdot117\,(2)$, $b = 12\cdot183\,(5)$, $c = 14\cdot633\,(5)$ Å, $M_r = 269\cdot1$, $V = 1090\cdot5$ Å^3, $Z = 4$, $D_m = 1\cdot64$, $D_x = 1\cdot64$ Mg m^{-3}, μ(Mo $K\alpha$, $\lambda = 0\cdot71069$ Å) $= 1\cdot29$ mm^{-1}, final $R = 0\cdot037$ and $R_w = 0\cdot032$ for 1601 non-zero reflexions. The Mn atom is octahedrally coordinated by one carboxylate O atom and one hydroxyl O atom from each lactate ligand and two water O atoms in *cis* positions. In this way neutral molecules $[Mn(CH_3CHOHCOO)_2(H_2O)_2]$ are formed which are held together through hydrogen bonds. Mn—O distances range between 2·146 (3) and 2·185 (2) Å.

Introduction. This investigation was undertaken as part of a study on the stereochemistry of Mn carboxylate salts. Preliminary data of the crystal structures of racemic Zn^{II} and Mn^{II} lactate trihydrates have been reported by Singh, Jain, Sakore & Biswas (1975), who have solved the structure of the Zn salt and have found both salts to be isotypic.

Single crystals of $Mn(C_3H_5O_3)_2.2H_2O$ were prepared by dissolving Mn^{II} carbonate in a commercially available L-lactic acid, and allowing the solution to evaporate. Nearly colorless crystals grew as orthorhombic needles or plates. Weissenberg photographs showed the space group to be $P2_12_12_1$. A

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