GERMAIN, G., MAIN, P. & WOOLFSON, M. M. (1970). *Acta Cryst.* B**26**, 274–285.
GERMAIN, G. & WOOLFSON, M. M. (1968). *Acta Cryst.* B**24**, 91–96.
International Tables for X-ray Crystallography (1974). Tome IV, pp. 71–78. Birmingham: Kynoch Press.
JAULMES, S. & JULIEN-POUZOL, M. (1977). *Acta Cryst.* B**33**, 1191–1193.
MEULENAER, J. DE & TOMPA, H. (1965). *Acta Cryst.* **19**, 1014–1018.
NIIZEKI, N. & BUERGER, M. J. (1957). *Z. Kristallogr.* **109**, 161–183.

Acta Cryst. (1981). B**37**, 1284–1286

Structure of Pyridinium *catena*-μ-Chloro-chloro(3,4,5,6-tetrachloropyrocatecholato)antimonate(III)

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Abstract. $[C_5H_6N]^+[Sb(C_6Cl_4O_2)Cl_2]^-$, $M_r = 518\cdot6$, monoclinic, $a = 14\cdot051\,(9)$, $b = 8\cdot494\,(6)$, $c = 16\cdot508\,(11)$ Å, $\beta = 98\cdot21\,(5)^\circ$, $V = 1950\cdot02$ Å^3, $D_c = 1\cdot77$ for $Z = 4$, $D_m = 1\cdot75$ Mg m^{-3} (displacement of chlorobenzene), $F(000) = 992$; systematic absences $h0l$ for $l = 2n$, space group $P2_1/c$. $R = 0\cdot081$ for 1882 reflections. The Sb atoms have three short bonds: Sb—O 2·051 (11) and 2·065 (17) Å; and Sb—Cl 2·469 (9) Å. Five-coordination is completed by two bridging Sb—Cl contacts [2·873 (10) and 3·001 (9) Å]. The pyridinium ion is hydrogen bonded to one of the O atoms of the pyrocatechol groups.

Introduction. There are few reports on the determination of the crystal structures of pyrocatechol derivatives of main-group elements. In particular, the structure of only one Sb^{III} derivative, antimony pyrogallate, is known (Aurivillius & Särnstrand, 1976). We now report the structure of the title compound.

Tetrachloropyrocatechol (0·01 mol) in 25 ml of dry methanol was added to $SbCl_3$ (0·01 mol) in 25 ml of dry methanol and the mixture refluxed for 2 h under nitrogen. Pyridine (0·01 mol) was added slowly to the cooled reaction mixture. The precipitate was filtered, washed with dry methanol followed by petroleum ether and then dried. The product was recrystallized from acetonitrile to give crystals which melted at 482–483 K. Analysis gave Sb 22·6, Cl 38·9%. Values required for $[C_5H_6N]^+[Sb(C_6Cl_4O_2)Cl_2]^-$ are Sb 22·7, Cl 39·1%.

Single-crystal rotation and Weissenberg photographs of a crystal mounted along **b** were obtained and the cell dimensions deduced from them. These values were then used as the basis for a least-squares refinement of measurements from a Debye–Scherrer powder photograph.

Intensities were collected from a crystal (mean diameter 0·30 mm) mounted along **b** on a Nonius equi-inclination integrating Weissenberg camera with Zr-filtered Mo $K\alpha$ radiation ($\lambda = 0\cdot7107$ Å). The 1882 reflections which were collected for layers 0 to 6 were measured on a Nonius Mk II microdensitometer. No absorption corrections were made ($\mu R = 0\cdot381$).

The positions of the Sb atoms were determined from a Patterson synthesis and refined by full-matrix least squares before those of the Cl atoms were obtained from a Fourier synthesis. The positions of the O atoms and finally of the C and N atoms were obtained from Fourier and difference syntheses phased on the Sb and Cl positions.

Full-matrix least-squares refinement of layer scale factors, atomic positions, anisotropic temperature factors for Sb and Cl and isotropic temperature factors for O, C and N converged with $R = \sum |F_o| - |F_c|/\sum |F_o| = 0\cdot081$ with unit weights. Scattering factors for neutral Sb, Cl, O, C and N were taken from *International Tables for X-ray Crystallography* (1962).

The final atomic coordinates are given in Table 1, bond distances and angles in Table 2.*

The computer programs used were *NUCLS*4 (J. A. Ibers & R. J. Doedens), *FORDAP* (A. Zalkin; personal communication, D. Bright), *ORFFE* (Busing, Martin & Levy, 1964), and *CELLPLOT* (Puxley & Donaldson, 1973).

Discussion. The structure consists of chains of $[Sb(C_6Cl_4O_2)Cl_2]$ units linked by bridging Cl atoms. The

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35614 (19 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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chains are anionic and the charge is balanced by discrete pyridinium cations. The arrangement of two of the four fomula units in the cell is shown in Fig. 1.

The environment of the Sb^{III} atom (Fig. 2) consists of two short Sb—O bonds (2·051 and 2·065 Å), one short Sb—Cl bond (2·469 Å) and two longer Sb—Cl distances (2·873 and 3·001 Å) to bridging Cl atoms. This gives a trigonal-bipyramidal arrangement of short nearest-neighbour bonds around Sb with the two longer Sb—Cl distances completing a distorted five-coordinated environment in which a sterically active lone pair completes a distorted octahedral distribution of electron pairs. It is possible to pick out from the Sb environment a trigonal-bipyramidal distribution of nearest-neighbour atoms similar to those found in cubic (Svensson, 1975) and orthorhombic (Svensson, 1974) Sb_2O_3 or in $SbCl_3$ (Lindqvist & Niggli, 1956). The bond lengths are greater than the corresponding ones in cubic Sb_2O_3 (1·977 Å), orthorhombic Sb_2O_3 (1·98, 2·02, 2·02 Å) and $SbCl_3$ (2·36 Å). The lengthening of the Sb—O and Sb—Cl bonds in the tetrachloropyrocatechol complex is clearly associated with an increase in the coordination of the Sb by the two bridging Cl atoms. Such lengthening of bonds (Table 3) is a common feature in both Sb—O and Sb—Cl compounds in which the Sb coordination is greater than three. Similar effects have been noted in the structural chemistry of Sn^{II}, which is isoelectronic with Sb^{III}. In Sn^{II} an increase in the metal coordination from the usual trigonal-bipyramidal environment only occurs if at least one of the three short bonds is lengthened (Dewan, Silver, Andrews, Donaldson & Laughlin, 1977; Donaldson, Donoghue & Smith, 1976). In Sn^{II} structures this often leads to four-coordinated environ-

Table 1. *Final atomic parameters with e.s.d.'s in parentheses*

	x	y	z	B_{eq}/B (Å^2)*
Sb	0·0950 (1)	0·0754 (2)	0·1701 (1)	3·11
Cl(1)	−0·0071 (6)	0·3078 (12)	0·2642 (4)	5·68
Cl(2)	0·1999 (5)	0·2817 (11)	0·1254 (4)	5·24
Cl(3)	0·3522 (5)	−0·3026 (11)	0·1108 (4)	5·09
Cl(4)	0·5143 (5)	−0·3380 (12)	0·2615 (5)	5·73
Cl(5)	0·4923 (4)	−0·1702 (11)	0·4250 (4)	5·17
Cl(6)	0·3107 (4)	0·0382 (10)	0·4369 (3)	4·03
O(1)	0·1821 (9)	0·0638 (21)	0·2808 (7)	2·67 (2)
O(2)	0·1939 (9)	−0·0896 (23)	0·1436 (8)	3·18 (3)
C(1)	0·2543 (13)	−0·0251 (30)	0·2800 (10)	2·41 (3)
C(2)	0·2641 (13)	−0·1139 (31)	0·2062 (11)	2·67 (4)
C(3)	0·3430 (14)	−0·2102 (33)	0·2003 (12)	3·04 (4)
C(4)	0·4146 (15)	−0·2284 (35)	0·2698 (13)	3·55 (4)
C(5)	0·4044 (14)	−0·1472 (31)	0·3425 (11)	2·88 (4)
C(6)	0·3256 (13)	−0·0521 (33)	0·3457 (11)	2·84 (4)
C(7)	0·3757 (30)	0·0913 (72)	−0·1109 (26)	9·88 (11·1)
C(8)	0·3066 (28)	0·0906 (64)	−0·1838 (23)	8·41 (9)
C(9)	0·2195 (31)	0·0319 (70)	−0·1807 (25)	9·70 (11·4)
C(10)	0·1905 (25)	0·0219 (59)	−0·0971 (22)	7·94 (9)
C(11)	0·3447 (35)	0·0278 (81)	−0·0274 (28)	10·86 (13·1)
N	0·2533 (24)	0·0046 (50)	−0·0269 (18)	6·55 (7)

* For Sb and Cl atoms $B_{eq} = \frac{4}{3}\sum_i \sum_j b_{ij}\,\mathbf{a}_i.\mathbf{a}_j$.

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

Sb—Cl(1)	3·001 (9)	C(6)—C(1)	1·39 (2)
Sb—Cl(1′)	2·873 (10)	C(3)—Cl(3)	1·694 (23)
Sb—Cl(2)	2·469 (9)	C(4)—Cl(4)	1·704 (26)
Sb—O(1)	2·051 (11)	C(5)—Cl(5)	1·714 (19)
Sb—O(2)	2·065 (17)	C(6)—Cl(6)	1·728 (22)
C(1)—O(1)	1·267 (26)		
C(2)—O(2)	1·338 (21)	C(7)—C(8)	1·43 (5)
C(1)—C(2)	1·46 (3)	C(8)—C(9)	1·33 (6)
C(2)—C(3)	1·39 (3)	C(9)—C(10)	1·50 (6)
C(3)—C(4)	1·42 (3)	C(10)—N	1·36 (5)
C(4)—C(5)	1·41 (3)	N—C(11)	1·30 (6)
C(5)—C(6)	1·38 (3)	C(11)—C(7)	1·60 (7)

Cl(1)—Sb—O(1)	80·8 (5)	C(2)—C(3)—C(4)	119·1 (2·0)
Cl(1′)—Sb—O(1)	81·9 (5)	Cl(4)—C(4)—C(3)	119·3 (1·8)
Cl(2)—Sb—O(2)	88·3 (5)	Cl(4)—C(4)—C(5)	121·4 (1·5)
O(1)—Sb—O(2)	79·7 (6)	C(3)—C(4)—C(5)	119·2 (2·1)
Cl(1)—Sb—Cl(1′)	93·6 (3)	Cl(5)—C(5)—C(4)	118·1 (1·7)
Cl(1)—Sb—Cl(2)	92·1 (3)	Cl(5)—C(5)—C(6)	121·9 (1·6)
Sb—O(1)—C(1)	113·4 (11)	C(4)—C(5)—C(6)	120·0 (1·7)
Sb—O(2)—C(2)	112·7 (1·3)	Cl(6)—C(6)—C(1)	116·3 (1·7)
O(1)—C(1)—C(2)	119·3 (1·5)	Cl(6)—C(6)—C(5)	119·5 (1·3)
O(1)—C(1)—C(6)	125·5 (1·8)	C(1)—C(6)—C(5)	124·2 (1·9)
C(2)—C(1)—C(6)	115·1 (1·9)	C(8)—C(7)—C(11)	119·2 (3·8)
O(2)—C(2)—C(1)	114·7 (1·8)	C(7)—C(8)—C(9)	119·1 (4·0)
O(2)—C(2)—C(3)	122·9 (1·8)	C(8)—C(9)—C(10)	115·5 (3·6)
C(1)—C(2)—C(3)	122·3 (1·6)	C(9)—C(10)—N	124·3 (3·3)
Cl(3)—C(3)—O(2)	119·6 (1·4)	C(10)—N—C(11)	120·0 (3·6)
Cl(3)—C(3)—C(4)	121·3 (1·8)	C(7)—C(11)—N	116·6 (3·6)

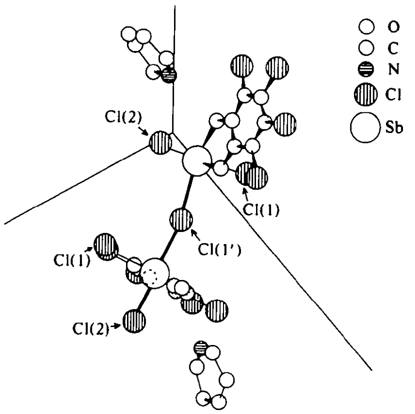

Fig. 1. Structure of the title compound.

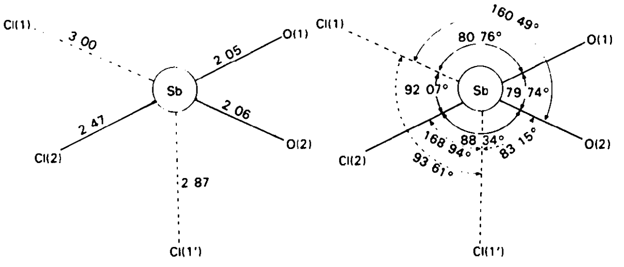

Fig. 2. The environment of the Sb atoms.

Table 3. *Compounds containing* Sb—O *bonds*

Compound	Bond distances (Å)	Bond angles (°)
Sb_2O_3 (cubic)	1·977	95·6, 95·9
Sb_2O_3 (orthorhombic)	1·98, 2·02, 2·02	79·8
$Sb(C_6H_3O_3).H_2O$	2·022, 2·23	78·0, 82·7, 92·9
$Fe(C_{12}H_8N_2)_3(C_4H_6O_2Sb)_2.H_2O$	1·94, 2·11, 2·16	79·7, 82·7, 84·8, 100·3
$K_2[Sb_2(C_4H_2O_6)_2].3H_2O$ (racemic)		
[Sb(1)]	2·05, 2·06, 2·25, 2·17	77·0, 77·5, 78·9, 82·0
[Sb(2)]	1·91, 2·01, 2·16, 2·22	78·5, 79·7, 80·5, 85·6
$K_2[Sb_2\{(+)\text{-}C_4H_2O_6\}_2].3H_2O$		
[Sb(1)]	1·97, 2·00, 2·13, 2·18	77·8, 78·6, 101·4, 147·7
[Sb(2)]	1·99, 2·01, 2·12, 2·21	77·2, 79·5, 101·1, 148·8
$SbNbO_4$	2·008, 2·038, 2·134, 2·331	92·1, 150·7
$(NH_4)_3Sb(C_2O_4)_3.4H_2O$	2·06, 2·16 (axial) 2·26, 2·32 (equatorial)	70–72
$[Sb(C_6Cl_4O_2)Cl_2]^-[C_5H_6N]^+$	2·051, 2·065	79·7

ments with two short and two longer bonds. This type of coordination is also found in many Sb^{III} compounds such as $Sb(C_6H_3O_3).H_2O$ (Aurivillius & Särnstrand, 1976), $Fe(C_{12}H_8N_2)_3(C_4H_2O_6Sb)_2.8H_2O$ (Zalkin, Templeton & Ueki, 1973), $K_2[Sb_2(C_4H_2O_6)_2]$ (Kamenar, Grdenić & Prout, 1970; Gress & Jacobson, 1974), $SbNbO_4$ (Skapski & Rogers, 1965), $SbCl_3.NH_2C_6H_5$ (Hulme & Scruton, 1968) and $C_5H_5NH.SbCl_4$ (Porter & Jacobson, 1970). In Sb^{III} chloride complexes such as $(NH_4)_2SbCl_5$ (Webster & Keats, 1971) and K_2SbCl_5 (Wismer & Jacobson, 1974), in which the coordination of the Sb is raised to five, only Sb—Cl bonds of length comparable with the short bonds in $SbCl_3$ remain. Similar lengthening of the Sb—O bond is found in the five-coordinate environment of $(NH_4)_3Sb(C_2O_4)_3.4H_2O$ (Poore & Russell, 1971). The Sb—O bonds in the title compound fall within the range of the short Sb—O bonds found in the compounds with coordination greater than three, *viz.* 1·91–2·07 Å, but the short Sb—Cl bond is significantly longer than the shortest Sb—Cl bonds (2·32–2·38 Å). This suggests that it is the Sb—Cl rather than the Sb—O bond that is weakened because of the formation of the bridging Cl bonds.

References

AURIVILLIUS, B. & SÄRNSTRAND, C. (1976). *Acta Chem. Scand.* **30**, 232–234.

BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1964). *ORFFE*. Report ORNL-TM-306. Oak Ridge National Laboratory, Tennessee.

DEWAN, J. C., SILVER, J., ANDREWS, R. H., DONALDSON, J. D. & LAUGHLIN, D. R. (1977). *J. Chem. Soc. Dalton Trans.* pp. 368–371.

DONALDSON, J. D., DONOGHUE, M. T. & SMITH, C. H. (1976). *Acta Cryst.* B**32**, 2098–2101.

GRESS, M. E. & JACOBSON, R. A. (1974). *Inorg. Chim. Acta*, **8**, 209–217.

HULME, R. & SCRUTON, J. C. (1968). *J. Chem. Soc.* pp. 2448–2452.

International Tables for X-ray Crystallography (1962). Vol. III, pp. 201–212. Birmingham: Kynoch Press.

KAMENAR, B., GRDENIĆ, D. & PROUT, C. K. (1970). *Acta Cryst.* B**26**, 181–188.

LINDQVIST, I. & NIGGLI, A. (1956). *J. Inorg. Nucl. Chem.* **2**, 345–347.

POORE, M. C. & RUSSELL, D. R. (1971). *Chem. Commun.* pp. 18–19.

PORTER, S. K. & JACOBSON, R. A. (1970). *J. Chem. Soc. A*, pp. 1356–1359.

PUXLEY, D. C. & DONALDSON, J. D. (1973). *Acta Cryst.* A**29**, 91–93.

SKAPSKI, A. C. & ROGERS, D. (1965). *Chem. Commun.* pp. 611–613.

SVENSSON, C. (1974). *Acta Cryst.* B**30**, 458–461.

SVENSSON, C. (1975). *Acta Cryst.* B**31**, 2016–2018.

WEBSTER, M. & KEATS, S. (1971). *J. Chem. Soc. A*, pp. 298–299.

WISMER, R. A. & JACOBSON, R. A. (1974). *Inorg. Chem.* **13**, 1678–1680.

ZALKIN, A., TEMPLETON, D. H. & UEKI, T. (1973). *Inorg. Chem.* **12**, 1641–1646.