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Guanidinium Pentafluoroantimonate

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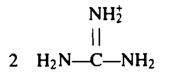
Abstract

The structure of diguanidinium pentafluoroantimonate, $(CH_6N_3)_2[SbF_5]$, has been determined and refined to $R = 2.3\%$. The SbF_5^{2-} anion is a distorted rectangular pyramid with F atoms at the vertices and a mirror plane C_s through atoms F(1) and Sb. The two inequivalent guanidinium ions are planar and display only mirror symmetry, not C_3, as expected. The crystal structure consists of two sets of guanidinium sheets linked by N—H···F hydrogen bonds to pentafluoroantimonate ions.

Comment

Various guanidinium salts such as guanidinium hexafluorogallate (Małuszyńska, 1993; Kozak, Grottel & Pająk, 1993) and guanidinium nitrate (Katrusiak & Szafrański, 1993; Wąsicki, Grottel & Pająk, 1994) have been studied by X-ray and NMR methods. In the crystal structures of these salts, different types of ion motions and phase transitions in a large temperature range have been observed. The guanidinium ion usually undergoes a reorientation around the C_3 symmetry axis. The motions of the anions depend greatly on their symmetry, shape and environment.

In the title compound, (I), the SbF_5^{2-} ion is a distorted rectangular pyramid and its geometry agrees with that reported by Ryan & Cromer (1972). It has only C_s crystallographic symmetry with the Sb atom 0.395 Å below the plane of the basal F(2) and F(3) atoms. The axial Sb—F(1) distance is significantly shorter than the basal Sb—F(2) and Sb—F(3) distances, as observed in ions and molecules isoelectronic with $SbF_5{}^{2-}$ (Ryan & Cromer, 1972, and references therein). The pyramids are related by a center of symmetry with an Sb···Sb distance of 4.191 Å.



$$2\ H_2N{-}\overset{\overset{\displaystyle NH_2^+}{\|}}{C}{-}NH_2\qquad [SbF_5]^{2-}$$

(I)

The two inequivalent guanidinium cations are planar and display only crystallographic mirror symmetry perpendicular to the guanidinium plane. All H atoms are involved in rather strong N—H···F hydrogen bonds (see Table 3). The axial F(1) atom is the weakest hydrogen-bond acceptor. The N···F distances of the basal F atoms range from 2.827 to 2.984 Å, while those of the axial F(1) atom range from 3.209 to 3.226 Å.

The packing in the crystal structure, shown in Fig. 2, consists of two sets of guanidinium sheets interconnected through the SbF_5^{2-} ions by hydrogen bonds.

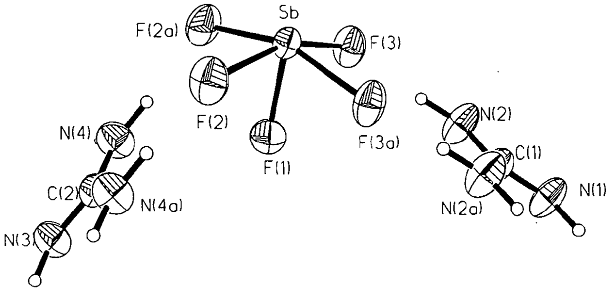


Fig. 1. *ORTEP* (Johnson, 1965) drawing of guanidinium pentafluoroantimonate with displacement ellipsoids at the 50% probability level.

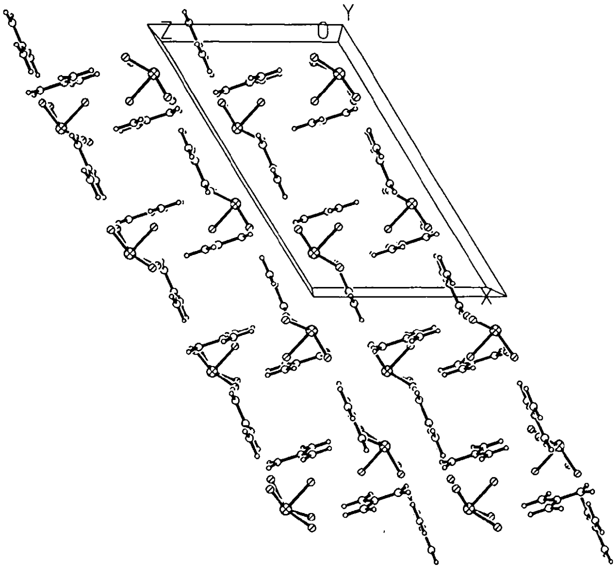


Fig. 2. Molecular packing diagram of the title compound viewed down the *y* axis.

Within each set, guanidinium ions are parallel but displaced. The shortest distance between the parallel guanidinium planes is 3.629 Å for Gu1, which contains atoms C(1), N(1) and N(2), and 4.884 Å for Gu2, with displacements of 1.99 and 1.83 Å for Gu1 and Gu2, respectively. The dihedral angles between the (001) plane and the two guanidinium ion planes are 8.3° for Gu1 and 76.6° for Gu2 with an angle between the guanidinium planes of 84.9°.

Experimental

Diguanidinium pentafluoroantimonate was obtained following the reaction

$$[C(NH_2)_3]_2CO_3 + 2HF + SbF_3 \rightarrow [C(NH_2)_3]_2[SbF_5] + CO_2 + H_2O$$

and recrystallized from 90% ethanol.

Crystal data

$(CH_6N_3)_2[SbF_5]$
$M_r = 336.9$
Monoclinic
$C2/m$
$a = 15.900\ (4)$ Å
$b = 8.456\ (2)$ Å
$c = 9.725\ (3)$ Å
$\beta = 121.19\ (2)°$
$V = 1118.5\ (5)$ Å^3
$Z = 4$
$D_x = 2.001$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 15 reflections
$\theta = 10.1–12.3°$
$\mu = 2.526$ mm^{-1}
$T = 295$ K
Needle
0.7 × 0.6 × 0.3 mm
Transparent

Data collection

Syntex $P2_1$ diffractometer
$\theta/2\theta$ scans
Absorption correction: empirical (*DIFABS*; Walker & Stuart, 1983)
$T_{min} = 0.79$, $T_{max} = 1.24$
3005 measured reflections
1640 independent reflections
1640 observed reflections $[F > 3.0\sigma(F)]$

$R_{int} = 0.0276$ on F after *DIFABS*
$\theta_{max} = 30.0°$
$h = -22 \rightarrow 22$
$k = 0 \rightarrow 15$
$l = -15 \rightarrow 15$
2 standard reflections monitored every 50 reflections
intensity variation: ±3%

Refinement

Refinement on F
$R = 0.0231$
$wR = 0.0314$
$S = 1.91$
1640 reflections
79 parameters
H atoms refined isotropically
$w = 1/[\sigma^2(F_o) + 0.0001F_o^2]$

$(\Delta/\sigma)_{max} = 0.004$
$\Delta\rho_{max} = 0.54$ e Å^{-3}
$\Delta\rho_{min} = -0.86$ e Å^{-3}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Sb	0.15398 (1)	1/2	0.13674 (2)	0.0324 (1)
F(1)	0.2573 (2)	1/2	0.3593 (3)	0.0488 (8)
F(2)	0.1022 (1)	0.6688 (2)	0.2308 (2)	0.0560 (8)
F(3)	0.2490 (1)	0.3327 (2)	0.1334 (2)	0.0522 (8)
C(1)	0.4853 (2)	1/2	0.1990 (4)	0.041 (1)
C(2)	0.1861 (2)	1/2	0.6457 (4)	0.040 (1)
N(1)	0.5750 (2)	1/2	0.2209 (5)	0.055 (2)
N(2)	0.4407 (2)	0.3637 (3)	0.1866 (4)	0.058 (1)
N(3)	0.2161 (3)	1/2	0.8033 (4)	0.051 (1)
N(4)	0.1612 (2)	0.3637 (3)	0.5699 (3)	0.053 (1)

Table 2. *Selected geometric parameters* (Å, °)

Atoms labelled with a prime (′) are symmetry-related atoms.

Sb—F(1)	1.924 (2)	C(1)—N(2)	1.326 (3)
Sb—F(2)	2.081 (2)	C(1)—N(2)′	1.326 (3)
Sb—F(2)′	2.081 (2)	C(2)—N(3)	1.349 (5)
Sb—F(3)	2.082 (2)	C(2)—N(4)	1.322 (3)
Sb—F(3)′	2.082 (2)	C(2)—N(4)′	1.322 (3)
C(1)—N(1)	1.328 (6)		
F(1)—Sb—F(2)	78.9 (1)	F(3)—Sb—F(3)′	85.6 (1)
F(1)—Sb—F(3)	79.2 (1)	F(2)′—Sb—F(3)′	158.1 (1)
F(2)—Sb—F(3)	158.1 (1)	N(1)—C(1)—N(2)	119.2 (2)
F(1)—Sb—F(2)′	78.9 (1)	N(1)—C(1)—N(2)′	119.6 (2)
F(2)—Sb—F(2)′	86.6 (1)	N(2)—C(1)—N(2)′	120.8 (4)
F(3)—Sb—F(2)′	89.8 (1)	N(3)—C(2)—N(4)	119.3 (2)
F(1)—Sb—F(3)′	79.3 (1)	N(3)—C(2)—N(4)′	119.3 (2)
F(2)—Sb—F(3)′	89.8 (1)	N(4)—C(2)—N(4)′	121.4 (4)

Table 3. *Hydrogen-bonding geometry* (Å, °)

D—H···A	H···A	D···A	D—H···A
N(1)—H(1)···F(2^{i})	1.93	2.828 (2)	146
N(2)—H(2)···F(3^{iii})	1.82	2.827 (4)	173
N(2)—H(21)···F(2^{ii})	2.01	2.890 (4)	143
N(3)—H(3)···F(3^{iii})	1.97	2.872 (2)	148
N(3)—H(3)···F(3^{iv})	2.54	3.292 (5)	131
N(4)—H(4)···F(2^{v})	1.89	2.899 (4)	172
N(4)—H(41)···F(1^{vi})	2.39	3.226 (3)	140
N(4)—H(41)···F(3^{vi})	2.13	2.984 (3)	142

Symmetry codes: (i) $x+\frac{1}{2}, \frac{3}{2}-y, z$; (ii) $\frac{1}{2}+x, y-\frac{1}{2}, z$; (iii) $\frac{1}{2}-x, \frac{1}{2}+y, 1-z$; (iv) $x, 1-y, 1+z$; (v) $x, 1-y, z$; (vi) $\frac{1}{2}-x, \frac{1}{2}-y, 1-z$.

Data collection: Syntex $P2_1$ software. Cell refinement: Syntex $P2_1$ software. Data reduction: *XTL/XTLE* (Syntex, 1976). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *SHELX*76 (Sheldrick, 1976). Molecular graphics: *XP* (Siemens, 1990).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry, including H-atom geometry, have been deposited with the IUCr (Reference: HU1085). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Tris(ethylmaltolato)bismuth(III)

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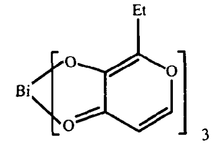
Abstract

The coordination around the Bi atom of the title compound, tris(2-ethyl-3-hydroxy-4*H*-pyran-4-onato-O^3,O^4)bismuth(III), [Bi($C_7H_7O_3$)$_3$], can be described as a distorted pentagonal bipyramid with five of the six coordinated O atoms approximately in the equatorial plane and the axial positions occupied by the sixth coordinated O atom and a stereoactive lone pair. This is a rare example of a six-coordinate Bi^{III} compound with a stereoactive lone pair.

Comment

The valence-shell electron-pair repulsion theory, VSEPR (Sidgwick & Powell, 1940; Gillespie & Nyholm, 1957), has proved an excellent guide to the stereochemistry of the *sp*-block elements towards the top of the Periodic Table and, indeed, for the halogens down to and including iodine. In this area non-bonding electron pairs are almost universally stereoactive. However, for the compounds and complexes of tin(II), antimony(III), bismuth(III) and tellurium(IV) the lone pair is commonly non-stereoactive (Wells, 1984). Examples of the relatively few bismuth(III) compounds with stereoactive lone pairs include Rb[Bi(SCN)$_4$] (Gałdecki, Główka & Goliński, 1976) and Bi(S_2COCH_3)$_3$ (Snow & Tiekink, 1987).

Tris(ethylmaltolato)bismuth(III), (1), was prepared by the addition of an acidic solution of bismuth(III) chloride to a methanolic solution of ethylmaltol (2-ethyl-3-hydroxy-4*H*-pyran-4-one) with the pH adjusted to be weakly alkaline. It provides a further example of a bismuth(III) stereoactive lone pair.



(1)

In the approximately pentagonal bipyramidal structure, five of the six coordinated O atoms occupying the equatorial sites are almost coplanar, with bond angles at the Bi atom in the range 69.6 (2)–73.3 (3)°. The Bi atom is displaced 0.35 Å out of the equatorial plane of the coordinated O atoms and away from the axial atom O(21), such that all six coordinated O atoms lie on one side of the Bi atom (Fig. 1). As a consequence of the displacement of the Bi atom from the plane, the angles between the equatorial O atoms and the axial O atom at Bi are all less than 90°. The molecule adopts pseudo-*m* symmetry, not imposed by crystallographic constraints, similar to that found in M(S_2COCH_3)$_3$ (M = Bi, Sb) (Snow & Tiekink, 1987). The maltolato group with axially coordinated atom O(21) occupies the pseudo mirror plane through the molecule with the terminal ethyl C atom C(21) the only atom not in the plane. Similarly, the terminal atoms C(1) and C(11) of the equatorial maltolato groups are not symmetrically sited in the otherwise

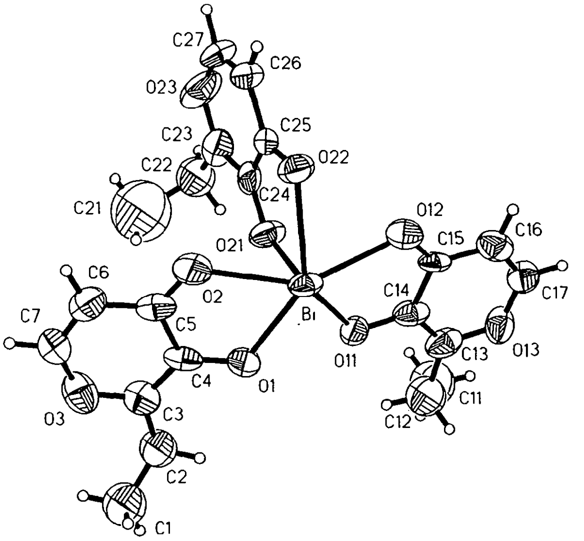


Fig. 1. Displacement ellipsoid plot (*SHELXTL/PC XP*; Sheldrick, 1990) of the title compound; anisotropic ellipsoids represent 50% probability levels, H atoms are represented as spheres of arbitrary radii.

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