

the angle C(2)–O(3)–O(5) as 139.6° is favourable for hydrogen bond formation. The other hydroxyl oxygen O(3) has only one intermolecular oxygen O(5) at a distance less than 3.4 \AA (Table 8) and a hydrogen bond is possible between these two. These possible hydrogen bonds have been indicated by dashed lines in Fig. 3.

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The Crystal Structure of Thallous Fluoride Carbonate

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The crystal structure of the title compound has been determined by single-crystal X-ray diffraction with 611 observed reflexions refined to an R value of 0.072. The crystals are monoclinic, space group $P2_1/m$ with $a = 7.510$, $b = 7.407$, $c = 6.069 \text{ \AA}$, $\gamma = 120.00^\circ$, $Z = 2$, $D_c = 7.86$. The structure is ionic and the three independent Tl^+ ions have almost identical environments, each with 7 neighbours in capped octahedral geometry. The Tl–O and Tl–F distances show the effect of a sterically active electron pair on Tl^+ . There are three long Tl–O (3.09 and 3.18 \AA twice, mean values) to oxygen atoms in one face of the octahedron. The opposite face has intermediate distances Tl–F 2.751 \AA (twice) and Tl–O 2.85 \AA , while the capping oxygen atom in the centre of this face has Tl–O 2.61 \AA . The packing is related to that of NiAs.

While attempting to grow crystals of thallous fluoride (Alcock, 1969 and in preparation) by slow evaporation in air of an ethanol/water (5:1) solution, a small number of chunky hexagonal-prismatic crystals were observed, very different from the thin flakes normal for thallous fluoride. The crystals were examined in the hope that they might be a less intractable modification of thallous fluoride, but they were eventually found to be a mixed fluoride–carbonate. However, as such their structure is of interest, both as an apparently novel structure type, with affinities with the NiAs structure, and as an instance of a stereochemically active ‘inert’ pair of electrons on the Tl^+ ion.

Experimental

Preparation

The characterization of this compound rests on the results of the structure analysis and is discussed below. The original sample of thallous fluoride was prepared by heating thallous carbonate with excess hydrofluoric acid, reducing to dryness and then heating to above the melting point; it had lattice constants identical with those reported for thallous fluoride. The mixed fluoride carbonate was then obtained as above. From the method of preparation it should have contained no carbonate and the only likely source for this is carbon

dioxide in the air. Attempts were made to crystallize thallos fluoride carbonate from solutions equimolar in thallos fluoride and carbonate in water and in ethanol/water, but the only product observed was thallos carbonate, the less soluble of the two salts. Presumably, the mixed salt forms only from solutions having some particular ratio of the two salts. Barlow & Meredith (1969), also observed hexagonal crystals from the ethanol/water recrystallization of thallos fluoride, which were probably the same as those characterized here.

Crystal data

Tl_3FCO_3 : $M=692.11$, monoclinic, $a=7.510(3)$, $b=7.407(3)$, $c=6.069(3)$ Å, $\gamma=120.00(3)^\circ$, $U=292.37$ Å³, $Z=2$, $F_{000}=540$; $D_c=7.86$ [cf. 7.85, the mean density of TlF , 8.54 (calc, Alcock, in preparation) and Tl_2CO_3 , 7.16 (Gmelin, 1940)]. $\mu=830.1$ for $\text{Mo K}\alpha$ ($\lambda=0.71069$ Å) which was used throughout. Systematic absences: $00l$, $l \neq 2n$ indicate space groups $P2_1/m$ or $P2_1$, of which the former was chosen on the basis of

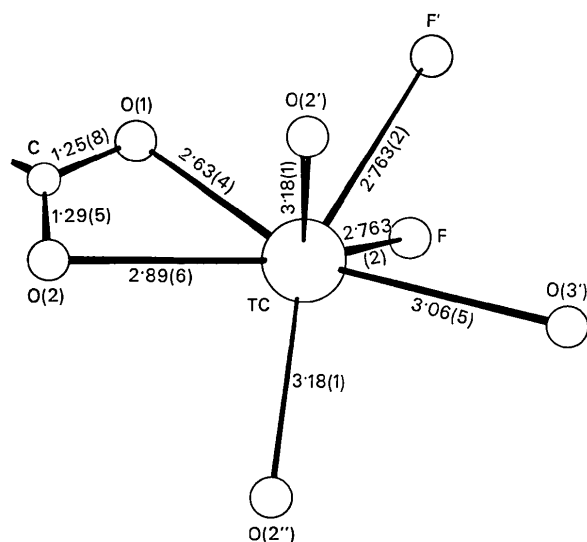


Fig. 1. Environment of the thallium atoms, using $\text{Tl}(2)$ as an example. The large face of the octahedron is at the right front and the capping atom, $\text{O}(1)$, is at the left rear. The view is approximately from (111) . The atomic numbering is as in Table 2 [under $\text{Tl}(2)$]. Large circle Tl , medium circles O and F , small circle C .

the structure determination. The general positional multiplicity is 4 in this space group and there are therefore limitations on possible atomic positions. In fact these take the form of each fluoride ion being on a centre of symmetry and the three thallos ions and the carbonate ion lying in mirror planes. The crystals are thick hexagonal plates, bounded by $\{001\}$ and $\{100\}$, $\{010\}$ and $\{1\bar{1}0\}$, which are often twinned on c . It was found that the crystals decomposed fairly rapidly, probably by hydrolysis, and their stability was improved by coating them with shellac. The unit cell was determined by a least-squares fitting of the exact reflecting positions of 12 high-angle reflexions, measured on a Picker FACS-1 diffractometer, and the errors given are those obtained in the least-squares refinement. Reflexion data were collected on this instrument with 4° take-off angle and a graphite monochromator in perpendicular geometry, using an ω scan of 1° with background counts of 20 sec at each end of the scan, to $2\theta=60^\circ$. Three check reflexions were used which showed a slight decrease in intensity with time, rather greater for high-angle than for low-angle reflexions. This was compensated for multiplying the intensity of the N th reflexion (observed at $2\theta_N$) by $1 + Nk_1 + Nk_2 2\theta_N$. $k_1=0.000111$ and $k_2=0.000005$ were chosen to fit the rate of decomposition. Lorentz and polarization corrections were applied assuming the monochromator to be ideally mosaic. 611 independent reflexions were considered to be observed with $I/\sigma(I) > 3$. An absorption correction was applied by the analytical method with the program *ABSCOR* in the X-RAY 63 system. The maximum and minimum transmission factors were 0.104 and 0.016.

The diffraction pattern showed marked pseudo-hexagonal symmetry; the Patterson synthesis had all its strong peaks with $W=0$ or 0.5, and these were readily interpreted for three thallium atomic positions, all in special position $2(e)$ of space group $P2_1/m$ ($x, y, \frac{1}{4}$; $\bar{x}, \bar{y}, \frac{3}{4}$) around a pseudo-threefold axis at $\frac{1}{2}, \frac{1}{2}, z$, as opposed to any of the other ways of placing six atoms in one unit cell in space group $P2_1/m$. Refinement showed the correctness of the solution and it was in fact refined to convergence at $R=0.103$ with anisotropic temperature factors, although possible light-atom positions were seen on difference syntheses at earlier stages. Examination of the structure showed two

Table 1. Atomic coordinates ($\times 10^4$) and anisotropic temperature factors ($\times 10^3$) with standard deviations in parentheses

The temperature factors have the form:

$$\exp [-2\pi^2(U_{11}a^{*2}h^2 + U_{22}b^{*2}k^2 + U_{33}c^{*2}l^2 + 2U_{12}a^*b^*hk + 2U_{23}b^*c^*kl + 2U_{13}a^*c^*hl)].$$

	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
$\text{Tl}(1)$	2500 (3)	1580 (3)	2500	21.4 (9)	22.1 (9)	30.0 (10)	7.6 (7)	0	0
$\text{Tl}(2)$	8417 (3)	5888 (3)	2500	21.5 (9)	22.3 (9)	26.6 (9)	5.1 (7)	0	0
$\text{Tl}(3)$	4074 (3)	7511 (3)	2500	18.8 (8)	25.1 (10)	33.3 (10)	5.5 (7)	0	0
F	5000	5000	0	84 (26)	48 (21)	34 (19)	23 (20)	-29 (21)	-14 (19)
C	8303 (65)	1574 (93)	2500	2 (17)	37 (29)	114 (63)	9 (19)	0	0
$\text{O}(1)$	6764 (53)	1815 (60)	2500	3 (13)	11 (17)	267 (110)	0 (12)	0	0
$\text{O}(2)$	10142 (55)	3170 (71)	2500	1 (14)	24 (20)	240 (97)	-5 (14)	0	0
$\text{O}(3)$	8114 (71)	-140 (54)	2500	57 (27)	7 (15)	72 (31)	20 (17)	0	0

'cavities'. The smaller, around $\frac{1}{2}, \frac{1}{2}, 0$, was surrounded by an octahedron of thallium atoms and the largest difference map peak was at its centre, with satisfactory distances to the thallium atoms of about 2.75 Å. A larger hole was centred on 0.83, 0.15, 0.25, in the mirror plane with a peak at the centre, but this peak was rather far from any thallium atoms (3.1 Å). It was surrounded by three other peaks of almost equal size, each at about 2.7 Å from two thallium atoms. These were the only significant peaks on the difference map. On the initial assumption (from the preparation) that the crystals were of thallos fluoride, this cavity should contain two fluoride ions, but no possible combination both accounted for the peaks observed and gave meaningful interatomic distances. It was then recognized that the distance (1.2 Å) between the central and outer atoms of the triangular array corresponded to that in the CO_3^{2-} ion and that the formulation of the crystals as Tl_3FCO_3 accounted for the difference peaks and gave correct stoichiometry. Refinement on this basis proceeded satisfactorily to a final R of 0.072, with anisotropic temperature factors for all atoms and with an isotropic extinction factor included (Larson, 1970), which reached a final value for r^* of 0.0035 (2). A weighting scheme of the form

$$\sigma^2(F) \sim 2 + 0.01F + 0.000002F^3$$

provided a necessary slight reduction in weight for large F values. A final difference synthesis showed no significant peaks, and a refinement in space group $P2_1$

Table 2. Bond lengths and angles with standard deviations in parentheses

For shifted atoms, the transformation given applies to the second atom. F' is at (0.5, 0.5, 0.5). Other primes have constant meaning *only* in the section of the list for one thallium atom.

Tl(1)-F and F'		2.737 (2) Å
Tl(1)-O(2')	($x-1, y, z$)	2.57 (6)
Tl(1)-O(3')	($x-1, y, z$)	2.88 (5)
Tl(1)-O(1)		3.12 (5)
Tl(1)-O(3'')	($1-x, -y, 1-z$)	3.17 (1)
Tl(1)-O(3''')	($1-x, -y, -z$)	3.17 (1)
F — Tl(1)-F'		67.34 (6)°
F — Tl(1)-O(2')		83.5 (7)
F — Tl(1)-O(3')		120.9 (7)
F — Tl(1)-O(1)		74.8 (6)
F — Tl(1)-O(3''')		139.3 (6)
F — Tl(1)-O(3''')		72.4 (6)
F' — Tl(1)-O(2')		83.5 (6)
F' — Tl(1)-O(3')		120.9 (7)
F' — Tl(1)-O(1)		74.8 (6)
F' — Tl(1)-O(3''')		72.4 (5)
F' — Tl(1)-O(3''')		139.3 (5)
O(2')-Tl(1)-O(3')		45 (1)
O(2')-Tl(1)-O(1)		153 (1)
O(2')-Tl(1)-O(3'')		98 (1)
O(2')-Tl(1)-O(3''')		98 (1)
O(3')-Tl(1)-O(1)		160 (1)
O(3')-Tl(1)-O(3'')		84 (1)
O(3')-Tl(1)-O(3''')		84 (1)
O(1)-Tl(1)-O(3'')		90 (1)
O(1)-Tl(1)-O(3''')		90 (1)
O(3'')-Tl(1)-O(3''')		146 (1)

Table 2 (cont.)

Tl(2)-F and F'		2.763 (2) Å
Tl(2)-O(1)		2.63 (4)
Tl(2)-O(2)		2.89 (6)
Tl(2)-O(3')	($x, 1+y, z$)	3.06 (5)
Tl(2)-O(2')	($2-x, 1-y, 1-z$)	3.18 (1)
Tl(2)-O(2'')	($2-x, 1-y, -z$)	3.18 (1)
F — Tl(2)-F'		66.62 (6)°
F — Tl(2)-O(1)		83.0 (8)
F — Tl(2)-O(2)		121.4 (5)
F — Tl(2)-O(3')		73.9 (7)
F — Tl(2)-O(2')		138.6 (8)
F — Tl(2)-O(2'')		72.7 (7)
F' — Tl(2)-O(1)		82.9 (8)
F' — Tl(2)-O(2)		121.4 (5)
F' — Tl(2)-O(3')		73.9 (7)
F' — Tl(2)-O(2')		72.7 (7)
F' — Tl(2)-O(2'')		138.6 (8)
O(1)-Tl(2)-O(2)		47 (1)
O(1)-Tl(2)-O(3')		152 (1)
O(1)-Tl(2)-O(2')		99 (1)
O(1)-Tl(2)-O(2'')		99 (1)
O(2')-Tl(2)-O(3')		160 (1)
O(2')-Tl(2)-O(2')		86 (1)
O(2')-Tl(2)-O(2'')		86 (1)
O(3')-Tl(2)-O(2')		88 (1)
O(3')-Tl(2)-O(2'')		88 (1)
O(2'')-Tl(2)-O(2'')		145 (1)
Tl(3)-F and F'		2.746 (2) Å
Tl(3)-O(3')	($x, 1+y, z$)	2.64 (4)
Tl(3)-O(1')	($x, 1+y, z$)	2.79 (4)
Tl(3)-O(2')	($x-1, y, z$)	3.09 (4)
Tl(3)-O(1'')	($1-x, 1-y, 1-z$)	3.19 (2)
Tl(3)-O(1''')	($1-x, 1-y, -z$)	3.19 (2)
F — Tl(3)-F'		67.09 (7)°
F — Tl(3)-O(3')		81.3 (9)
F — Tl(3)-O(1')		119.3 (8)
F — Tl(3)-O(2')		74.3 (9)
F — Tl(3)-O(1'')		140.2 (9)
F — Tl(3)-O(1''')		73.6 (9)
F' — Tl(3)-O(3')		81.3 (9)
F' — Tl(3)-O(1')		119.3 (8)
F' — Tl(3)-O(2')		74.3 (9)
F' — Tl(3)-O(1'')		73.6 (9)
F' — Tl(3)-O(1''')		140.2 (9)
O(3')-Tl(3)-O(1')		46 (1)
O(3')-Tl(3)-O(2')		151 (2)
O(3')-Tl(3)-O(1'')		98.6 (7)
O(3')-Tl(3)-O(1''')		98.6 (7)
O(1'')-Tl(3)-O(2')		163 (1)
O(1'')-Tl(3)-O(1'')		84.7 (7)
O(1'')-Tl(3)-O(1''')		84.7 (7)
O(2')-Tl(3)-O(1'')		90.1 (6)
O(2')-Tl(3)-O(1''')		90.1 (6)
O(1''')-Tl(3)-O(1''')		144 (1)
C — O(1)		1.25 (8) Å
C — O(2)		1.29 (5)
C — O(3)		1.21 (9)
O(1)-C — O(2)		121 (6)°
O(1)-C — O(3)		121 (4)
O(2)-C — O(3)		118 (6)

gave no significant shifts. The final atomic parameters are given in Table 1, interatomic distances and angles in Table 2, and structure factors in Table 3. Scattering factors including anomalous dispersion were from *International Tables for X-ray Crystallography* (1962). All computing was with the X-ray 63 and X-ray

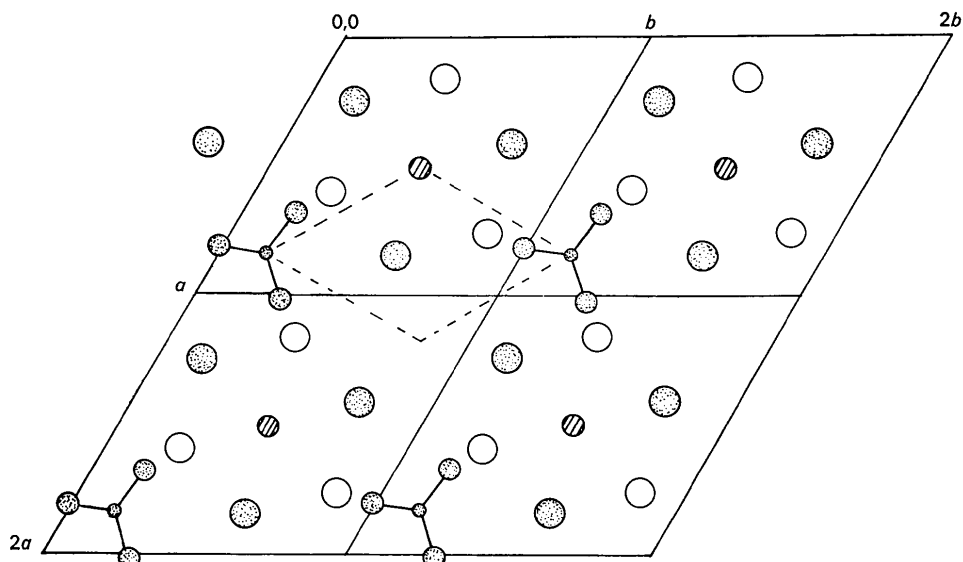


Fig. 2. Packing diagram viewed down c . Large circles Tl, medium circles O and F (line-shaded), small circles C. All the atoms at $z=0.25$ are shown stippled; the fluorine atoms ($z=0$ and 0.5) are line-shaded; only thallium atoms at $z=0.75$ (or -0.25) are shown as open circles. The dashed line outlines the pseudo cell analogous to that of NiAs.

by oxygen, thallos salicylate-phenanthroline (Hughes & Truter, 1972) and thallos ascorbate (Hughes & Truter, private communication). The former has Tl-O distances ranging from 2.65 to 3.00 Å, and the latter has similar distances. Another relatively complex structure is that of $Tl_4P_4O_{10}$ (Fawcett, Kocman, Nyburg & O'Brien, 1970) which has not been described in detail but in which the short Tl-O bonds (minimum 2.70 Å) all lie on one side of the Tl^+ ions.

Packing (Fig. 2)

The atomic arrangement is markedly pseudo-trigonal, with approximate threefold axes at $\frac{1}{2}, \frac{1}{2}, z$ and about $\frac{5}{6}, \frac{1}{6}, z$, passing through the fluorine and carbon atoms respectively. The thallos ions are approximately close-packed (*cf.* the atom at $z=0.25$ midway between the upper two carbonate groups in Fig. 2) but with systematic distortions. There are two sets of voids in the structure. The first contain fluorine atoms surrounded octahedrally. The second have the form of tricapped trigonal prisms and each is occupied by a carbonate ion.

There is an interesting resemblance between this structure and that of NiAs. A triple NiAs cell

$$\begin{pmatrix} 2 & 1 & 0 \\ -1 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

would have $c=5.0$ Å. $c/a=0.80$, as compared to $c=6.1$ and $c/a=0.81$ for a hexagonal approximation of the actual cell of Tl_3FCO_3 .

The thallos ions correspond to As in the NiAs structure apart from one major distortion. The latter structure can be considered as chains of octahedra running parallel to c and sharing parallel faces. One

such chain is preserved in Tl_3FCO_3 and contains fluoride ions at the centre of each octahedron (Fig. 2). For the other, pairs of octahedra are distorted by pulling out the central triangle of atoms, so that there is one large void with the form of a tri-capped trigonal prism instead of two smaller voids, and these are occupied by carbonate groups. They can be seen in Fig. 2 alternately with the three capping atoms stippled and the end atoms plain, and *vice versa*. This analogy with NiAs shows that Tl_3FCO_3 belongs to the group of close-packed structures even though it is more distorted than most members. One very significant difference between NiAs and Tl_3FCO_3 is that the longer c axis arising because Tl^+ is larger than As means that the distance $F^- - F^-$ is 3.03 Å in contrast to the 2.5 Å Ni-Ni which is short enough for bonded interactions.

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