thermal description for silver and one for iodine. These constraints are not imposed by the space group ($P6_3mc$) but no significant improvement in agreement of the data occurred when four independent positions were used.*

Discussion. The structure of the normal wurtzite phase has been described by Burley (1963). The present structure of AgI differs in one significant respect. Burley observed equal bond distances (2·814 and 2·813 Å) whereas in the 4*H* polytype there are three Ag–I bond distances of 2·811 (2) and one of 2·832 (6) Å. For both structures the thermal parameters for silver are considerably greater than those of iodine.

Other crystals of a pyramidal morphology were observed in the original preparation. These were found to be of the normal wurtzite type. No significant difference in impurity levels was detected for the two polytypes. Major impurities, as observed by emission spectroscopy analysis, were: Ca (10 p.p.m.), Cu and Si (5 p.p.m.), and Fe and Mg (3 p.p.m.).

This work was performed under the auspices of the U.S. Atomic Energy Commission.

---

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30864 (2 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

References

Burley, G. (1963). *J. Chem. Phys.* **38**, 2807–2812.
Cochrane, G. (1967). *Brit. J. Appl. Phys.* **18**, 687–688.
Prager, P. R. (1974). *Acta Cryst.* A**30**, 369–373.
Schock, R. N. & Hinze, E. (1975). To be published.

Acta Cryst. (1975). B**31**, 1483

Hexafluoroacetylacetonatothallium(I)

By S. Tachiyashiki and H. Nakayama
Kagawa Nutrition College, Sakado-machi, Saitama 350-02, *Japan*

and R. Kuroda, S. Sato and Y. Saito
The Institute for Solid State Physics, The University of Tokyo, Roppongi-7, Minato-ku, Tokyo 106, *Japan*

(*Received* 9 *November* 1974; *accepted* 26 *November* 1974)

Abstract. Tl(hfac), triclinic, $P\bar{1}$, $a=9{\cdot}576$ (8), $b=11{\cdot}320$ (8), $c=9{\cdot}445$ (6) Å, $\alpha=103{\cdot}86$ (5), $\beta=107{\cdot}28$ (8), $\gamma=67{\cdot}30$ (8)°. $Z=4$, $D_m=3{\cdot}06$, $D_x=3{\cdot}062$ g cm^{-3}, μ(Mo $K\alpha$) = 182·5 cm^{-1}. The structure consists of polymer chains formed by two different structural units linked by oxygen atoms of hfac anions along the *b* axis. Thallium ions are surrounded by five oxygen atoms. Three of these and the thallium ion lie approximately in a plane and the other two oxygen atoms are on one side of this plane. Tl–O distances range from 2·62 to 3·04 Å.

Introduction. Tl(hfac) is one of the most volatile 1:1 β-diketonato complexes. The crystal structure has been determined in order to gain a greater understanding of the stereochemistry of Tl and to reveal the packing mode of this volatile compound in crystals.

Crystals of Tl(hfac), prepared according to the method described by Hartman, Jacoby & Wojcicki (1970) and grown by sublimation, are thin pale yellow parallelepipeds. Unit-cell dimensions were determined from Weissenberg photographs and were later refined on a diffractometer. The intensities of reflexions were measured on a Rigaku automated four-circle diffractometer using Mo $K\alpha$ radiation ($\lambda=0{\cdot}7107$ Å) monochromated by a graphite plate. A crystal of dimensions $0{\cdot}12\times0{\cdot}15\times0{\cdot}15$ mm was used, coated with polycyanoacrylate resin to prevent sublimation. Out of 3931 accessible reflexions below $2\theta=55°$, 1835 with $|F|>3\sigma$ were used for the refinement. During the data collection, the intensities of standard reflexions decreased exponentially with time to 85% of the initial intensities, owing to sublimation and radiation damage. All the data were corrected for this effect.

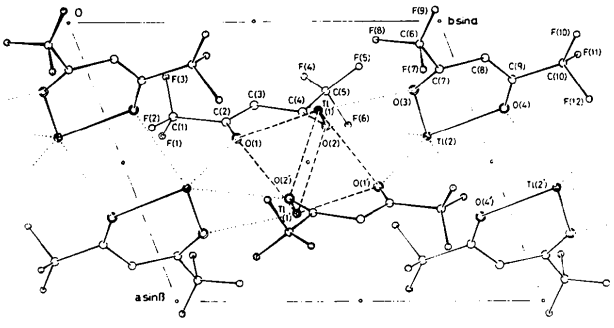

Fig. 1. A projection of the structure along the *c* axis.

Table 2. *Fractional atomic coordinates* (× 10^4 *for* Tl *atoms*, × 10^3 *for all other atoms*) *and thermal parameters, with estimated standard deviations*

The U_{ij}'s are defined by $\exp[-2\pi^2(U_{11}h^2a^{*2}+U_{22}k^2b^{*2}+U_{33}l^2c^{*2}+2U_{12}hka^*b^*+2U_{13}hla^*c^*+2U_{23}klb^*c^*)\times 10^{-3}]$.

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Tl(1)	3172 (2)	5803 (1)	5784 (2)	66 (1)	48 (1)	76 (1)	−17 (1)	32 (1)	9 (1)
Tl(2)	4085 (2)	8499 (1)	4058 (2)	77 (1)	40 (1)	66 (1)	−23 (1)	35 (1)	1 (1)
O(1)	415 (3)	335 (2)	379 (3)	80 (18)	60 (14)	77 (17)	−40 (13)	−7 (14)	15 (13)
O(2)	372 (3)	585 (2)	311 (2)	100 (19)	66 (14)	35 (13)	−17 (13)	16 (12)	20 (11)
O(3)	245 (2)	858 (2)	601 (2)	63 (15)	56 (13)	69 (15)	−9 (11)	35 (12)	11 (11)
O(4)	312 (3)	1084 (2)	550 (3)	97 (18)	44 (12)	133 (22)	−31 (13)	77 (17)	−12 (14)
C(1)	337 (5)	190 (3)	174 (5)	111 (34)	52 (21)	146 (42)	−49 (23)	47 (31)	−3 (24)
C(2)	357 (3)	322 (3)	244 (3)	35 (17)	56 (18)	46 (19)	−19 (14)	−14 (14)	16 (14)
C(3)	301 (5)	414 (3)	141 (4)	133 (33)	20 (13)	64 (22)	−30 (17)	26 (22)	10 (14)
C(4)	323 (4)	536 (3)	194 (3)	88 (25)	58 (19)	21 (16)	−36 (18)	−6 (16)	−6 (14)
C(5)	250 (5)	620 (3)	67 (4)	118 (32)	45 (18)	50 (21)	−37 (20)	8 (21)	−21 (16)
C(6)	83 (5)	918 (3)	767 (5)	136 (37)	35 (17)	122 (35)	4 (20)	84 (30)	10 (20)
C(7)	171 (3)	947 (2)	671 (3)	45 (18)	36 (15)	67 (20)	−17 (13)	35 (16)	−6 (14)
C(8)	135 (4)	1084 (3)	688 (4)	67 (22)	61 (19)	79 (24)	−34 (18)	34 (19)	19 (17)
C(9)	211 (4)	1137 (3)	626 (4)	92 (27)	34 (16)	97 (27)	−37 (17)	50 (23)	−18 (16)
C(10)	159 (5)	1286 (3)	660 (5)	96 (31)	44 (19)	113 (33)	−26 (20)	36 (26)	−13 (20)
F(1)	402 (5)	135 (3)	71 (4)	357 (52)	109 (22)	229 (38)	−129 (29)	212 (39)	−76 (23)
F(2)	382 (5)	112 (2)	262 (3)	334 (46)	95 (18)	106 (21)	−127 (25)	−22 (24)	54 (16)
F(3)	200 (4)	199 (3)	114 (6)	153 (32)	139 (29)	393 (65)	−86 (26)	−88 (36)	77 (36)
F(4)	205 (5)	574 (2)	−64 (3)	354 (46)	103 (19)	66 (17)	−132 (25)	−25 (22)	41 (14)
F(5)	167 (3)	733 (2)	102 (3)	168 (24)	60 (13)	115 (19)	15 (14)	69 (18)	44 (13)
F(6)	373 (4)	643 (3)	47 (4)	173 (31)	202 (34)	232 (39)	41 (25)	112 (29)	157 (31)
F(7)	177 (4)	902 (4)	900 (4)	218 (36)	382 (56)	148 (29)	−191 (39)	0 (25)	151 (34)
F(8)	73 (4)	805 (2)	723 (4)	249 (36)	78 (16)	280 (39)	−77 (20)	210 (33)	−24 (20)
F(9)	−40 (4)	995 (2)	792 (4)	192 (30)	95 (19)	296 (42)	15 (19)	196 (32)	64 (23)
F(10)	47 (3)	1351 (2)	723 (4)	168 (27)	60 (14)	305 (41)	−24 (16)	175 (29)	−9 (20)
F(11)	121 (4)	1336 (2)	533 (3)	283 (41)	56 (14)	136 (25)	−32 (20)	59 (26)	28 (16)
F(12)	278 (3)	1325 (2)	738 (4)	106 (20)	63 (14)	226 (31)	−45 (14)	68 (20)	−45 (17)

Corrections were also applied for Lorentz and polarization effects, but those for absorption and extinction were not made.

The structure was solved by routine application of the heavy-atom method and refined by the block-diagonal least-squares method using anisotropic thermal parameters. The R value decreased to 0·071 for the 1835 reflexions. A weighting scheme $w=1$ if $|F_o|>16{\cdot}6$ and $w=0{\cdot}5$ otherwise was employed. The atomic scattering factors and the correction for anomalous dispersion of the thallium atom were those listed in *International Tables for X-ray Crystallography* (1962). Observed and calculated structure factors are compared in Table 1.* Table 2 lists the final atomic parameters, together with their estimated standard deviations.

Discussion. A projection of the structure along the c axis is presented in Fig. 1. Interatomic distances and bond angles are listed in Table 3. Table 4 gives the equations of the mean planes of the hfac anions and the deviations of the atoms from them. There are two structural units in the crystal. One is a monomeric unit of Tl(hfac), where hfac(2) [O(3)–C(7)–C(8)–C(9)–O(4)] chelates to Tl(2) which lies 0·42 Å below the plane of the ligand. Tl–O distances of 2·62 and 2·72 Å in this unit are the shortest in this structure. They are, however, longer than those of 2·43 and 2·54 Å in acetylacetonatothallium(I) [Tl(acac)] (Webb, 1974). The other is a dimeric unit, in which one Tl(1)–hfac(1) [O(1)–C(2)–C(3)–C(4)–O(2)] and another related to the first by a centre of symmetry form an octahedron as shown in Fig. 2. Tl(1) deviates 1·56 Å from the plane of hfac(1). The Tl–Tl distance of 3·825 Å in this octahedron is shorter than other Tl–Tl separations of 4·199 and 4·246 Å, which may be compared with that of 3·84 Å observed in tetrameric thallium(I) methoxide (Dahl, Davis, Wampler & West, 1962). For the latter, a Tl–Tl interaction was suggested (Maroni & Spiro, 1968). Tl–O distances in this dimeric unit do not differ greatly from those outside the unit. The two structural units are linked to each other by their oxygen atoms to form a linear polymeric chain along the b axis. These chains are laterally packed, mainly by van der

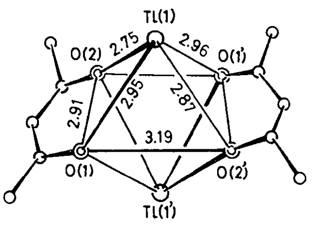

Fig. 2. A perspective view of the dimeric unit.

---

* Table 1 has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30794 (16 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 3. *Interatomic distances* (Å) *and bond angles* (°)

Tl(1)–Tl(1′)*	3·825 (3)	Tl(2)–Tl(2′)	4·199 (3)
Tl(1)–O(1)	2·95 (2)	Tl(1)–O(3)	2·91 (2)
Tl(1)–O(1′)	2·96 (3)	Tl(2)–O(2)	3·04 (3)
Tl(2)–O(3)	2·72 (3)	Tl(2)–O(1′)	2·94 (2)
Tl(2)–O(4′)	2·94 (3)	Tl(2)–O(4)	2·62 (2)
Tl(1)–Tl(2)	4·246 (3)	O(1)–Tl(1)–O(2)	61·3 (6)
Tl(1)–O(2)	2·75 (3)	O(3)–Tl(2)–O(4)	69·3 (6)
Tl(1)–O(2′)	2·87 (2)	O(1)–Tl(1′)–O(2)	59·7 (6)
hfac (1)			
O(1)—O(2)	2·91 (4)	C(2)—C(1)—F(1)	114 (4)
C(1)—C(2)	1·54 (5)	C(2)—C(1)—F(3)	113 (2)
C(4)—C(5)	1·55 (5)	C(4)—C(5)—F(5)	115 (3)
C(1)—F(3)	1·24 (6)	F(1)—C(1)—F(2)	106 (3)
C(5)—F(6)	1·37 (7)	F(3)—C(1)—F(1)	102 (4)
O(1)—C(2)	1·23 (4)	F(5)—C(5)—F(6)	100 (2)
C(2)—C(3)	1·44 (5)	O(1)—C(2)—C(1)	117 (2)
C(1)—F(1)	1·23 (7)	O(2)—C(4)—C(3)	134 (2)
C(5)—F(4)	1·24 (4)	C(1)—C(2)—C(3)	115 (2)
O(2)—C(4)	1·16 (3)	C(3)—C(4)—C(5)	110 (2)
C(3)—C(4)	1·43 (5)	C(2)—C(1)—F(2)	115 (3)
C(1)—F(2)	1·22 (6)	C(4)—C(5)—F(4)	121 (2)
C(5)—F(5)	1·24 (4)	C(4)—C(5)—F(6)	104 (3)
O(1)—C(2)—C(3)	129 (2)	F(2)—C(1)—F(3)	106 (4)
O(2)—C(4)—C(5)	116 (2)	F(4)—C(5)—F(5)	114 (2)
C(2)—C(3)—C(4)	119 (2)	F(6)—C(5)—F(4)	98 (3)
hfac (2)			
O(3)—O(4)	3·04 (4)	C(7)—C(6)—F(7)	107 (4)
C(6)—C(7)	1·57 (7)	C(7)—C(6)—F(9)	122 (3)
C(9)—C(10)	1·54 (4)	C(9)—C(10)–F(11)	110 (3)
C(6)—F(9)	1·22 (5)	F(7)—C(6)—F(8)	100 (2)
C(10)–F(12)	1·34 (5)	F(9)—C(6)—F(7)	105 (4)
O(3)—C(7)	1·17 (3)	F(11)–C(10)–F(12)	101 (3)
C(7)—C(8)	1·43 (4)	O(3)—C(7)—C(6)	116 (3)
C(6)—F(7)	1·32 (5)	O(4)—C(9)—C(8)	131 (2)
C(10)–F(10)	1·26 (6)	C(6)—C(7)—C(8)	109 (3)
O(4)—C(9)	1·25 (5)	C(8)—C(9)—C(10)	113 (3)
C(8)—C(9)	1·41 (7)	C(7)—C(6)—F(8)	111 (3)
C(6)—F(8)	1·28 (5)	C(9)—C(10)–F(10)	122 (3)
C(10)–F(11)	1·35 (6)	C(9)—C(10)–F(12)	111 (2)
O(3)—C(7)—C(8)	135 (3)	F(8)—C(6)—F(9)	110 (4)
O(4)—C(9)—C(10)	116 (3)	F(10)–C(10)–F(11)	104 (3)
C(7)—C(8)—C(9)	121 (3)	F(12)–C(10)–F(10)	106 (3)

* A prime indicates that the atom is related by a centre of symmetry to the unprimed atom.

Table 4. *Equations of mean planes of hfac anions and distances of atoms from the plane*

Atoms marked * were not included in mean-plane calculations.

Plane 1 $-0{\cdot}9160x+0{\cdot}3419y+0{\cdot}2100z+2{\cdot}2723=0$
Plane 2 $-0{\cdot}5226x+0{\cdot}2074y-0{\cdot}8270z+5{\cdot}0719=0$

Plane 1: hfac (1)		Plane 2: hfac (2)	
O(1)	0·007 Å	O(3)	0·031 Å
C(2)	−0·016	C(7)	−0·042
C(3)	0·020	C(8)	0·015
C(4)	−0·015	C(9)	0·013
O(2)	0·004	O(4)	−0·017
C(1)*	−0·064	C(6)*	−0·190
C(5)*	0·081	C(10)*	0·048
Tl(1)*	1·558	Tl(2)*	0·420
Tl(1′)*	−2·208		

Waals forces. This structural feature is different from that of Tl(acac), where discrete molecular units of Tl(acac) are linked infinitely along the *a* and *b* axes (Webb, 1974). The high volatility of Tl(hfac) compared with Tl(acac) would primarily be ascribed to the difference in the packing manner of the two compounds in the crystalline state. The oxygen atoms of the monomeric units coordinate to two thallium ions. This bridging interaction is similar to that observed in the Tl(sal.phen)* complex (Hughes & Truter, 1972). The oxygen atoms of the dimeric units coordinate to three thallium ions like those in tetrameric thallium(I) methoxide (Dahl, Davis, Wampler & West, 1962). Two different C=O stretching vibrational modes are observed at 1635 and 1652 cm^{-1} in the infrared spectra of this compound in the solid state. They may well be explained in terms of these two different types of oxygen atom. As shown in Fig. 1, the thallium ions are surrounded by five oxygen atoms. Three of these and Tl are in a plane and the two remaining oxygen atoms are deviated to one side of this plane. Tl–O distances are all less than 3·04 Å, which is the limit of the Tl–O coordination bond (Hughes, 1973). The arrangement of the oxygen atoms around the central Tl is not uniform and there are effectively no interacting atoms on one side of the coordination sphere. This indicates that the lone pair, originating from $6s^2$, is stereochemically active. The lone pair would possess some *p*-orbital character and occupy a large portion of the other side of the coordination sphere (Hughes, 1973). Accordingly, Tl–O bonds should possess considerable covalent character and in the valence-bond sense, the coordination geometry of Tl^{I} may be described as a highly distorted ψ octahedron.

The shapes and the sizes of hfac in the monomeric and dimeric units are similar and may be compared with those reported for other hfac complexes (Belford, Fenton & Truter, 1972). Both hfac groups are planar within the experimental errors.

Calculations were performed on the FACOM 270-30 of this Institute.

---

* Salicylato-phenanthroline.

References

Belford, R. C. E., Fenton, D. E. & Truter, M. R. (1972). *J. Chem. Soc. Dalton*, pp. 2208–2213 and references therein.

Dahl, L. F., Davis, G. L., Wampler, D. L. & West, R. (1962). *J. Inorg. Nucl. Chem.* **24**, 357–363.

Hartman, F. A., Jacoby, P. L. & Wojcicki, A. (1970). *Inorg. Synth.* **12**, 81–85.

Hughes, D. L. (1973). *J. Chem. Soc. Dalton*, pp. 2209–2215.

Hughes, D. L. & Truter, M. R. (1972). *J. Chem. Soc. Dalton*, pp. 2214–2219.

International Tables for X-ray Crystallography (1962). Vol. III. Birmingham: Kynoch Press.

Maroni, V. A. & Spiro, T. G. (1968). *Inorg. Chem.* **7**, 193–197.

Webb, N. C. (1974). Personal communication (see also Hughes, 1973).