

Table 3. *Hydrogen bonds*

O—H...O	O...O	H...O	∠O—H...O
O(7)—H(10)...O(3)	2.748 (12) Å	2.10 (15) Å	147 (10)°
O(7)—H(11)...O(5)	2.709 (7)	1.95 (8)	160 (13)
O(8)—H(12)...O(4)	2.734 (15)	2.05 (19)	161 (14)
O(8)—H(13)...O(10)	2.734 (11)	1.91 (9)	163 (15)
O(9)—H(14)...O(6)	2.764 (12)	1.91 (14)	162 (13)
O(9)—H(15)...O(2)	2.745 (11)	1.98 (11)	164 (16)
O(10)—H(16)...O(9)	2.888 (8)	2.11 (8)	169 (12)
O(10)—H(17)...O(9)	2.792 (16)	1.81 (14)	160 (9)

acetates while the tetrahydrate is the predominant form for Sm to Lu. The tetrahydrates are isostructural and crystallize in space group  $P\bar{1}$  (Vadura & Kvapil, 1971). We determined the structure of  $\text{Ho}(\text{C}_2\text{H}_3\text{O}_2)_3 \cdot 4\text{H}_2\text{O}$  whose structural details compare closely with those of the isostructural Er compound (Aslanov, Abdul'minev, Porai-Koshits & Ivanov, 1972).

The basic structural element consists of a centrosymmetric dimer formed by two  $\text{Ho}(\text{Ac})_3$  units and four water molecules. The link within the dimer is formed by O(1) which belongs to the coordination sphere of two Ho and by the water molecules O(7) and O(8). Two independent carboxyl groups are in the coordination sphere of only one Ho, and are bidentate; the other [with O(1)] is tridentate bridge-cyclic. The dimers are interconnected by water molecules O(9) and O(10). All hydrate H atoms are involved in medium to weak hydrogen bonds (Table 3).

Ho has a ninefold coordination of O atoms, seven from carboxyl groups, and two from water molecules. The Ho—O bonds to the water molecules are slightly shorter than those to the carboxyl groups. The C—O distances of 1.26 (2) to 1.28 (2) Å are normal for carboxyl groups. They do not confirm the results of

Aslanov *et al.* (1972) who report large differences within one carboxyl group [1.19 (4) and 1.35 (4) Å]. The O—C—O angles of 119 (1)° are rather small but not unusual. The shortest Ho—Ho distance within the dimer is 4.159 (2) Å. A superexchange *via* O(1) is possible between these two atoms, and may lead to possible magnetic ordering of the rare earths. Further distances of 6.222, 6.445 and 7.671 Å may involve supersuperexchange *via* carboxyl groups and water molecules. The measurement of the magnetic susceptibility, however, revealed paramagnetic behaviour between 4.2 and 300 K.

The X-ray measurements were performed at the Institut für Kernphysik der Universität Frankfurt by kind permission of Dr M. Müllner.

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### Bis( $\mu$ -trifluoroacetato-O,O')-bis[*dimethyltin*(IV)]

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**Abstract.**  $\text{Sn}_2(\text{CH}_3)_4(\text{C}_2\text{F}_3\text{O}_2)_2$ ,  $\text{C}_8\text{H}_{12}\text{F}_6\text{O}_4\text{Sn}_2$ ,  $M_r = 523.55$ , monoclinic, space group  $C2/m$ ,  $a = 14.887$  (5),  $b = 8.223$  (5),  $c = 7.518$  (3) Å,  $\beta = 118.84$  (2)°,  $D_x = 2.15$  Mg m<sup>-3</sup>,  $Z = 2$ . The structure was refined from 1027 diffractometer-measured X-ray

reflections to  $R_w = 0.042$ . The dimer is isostructural with  $\text{Sn}_2(\text{CH}_3)_4(\text{C}_2\text{H}_2\text{ClO}_2)_2$ , having crystallographic  $2/m$  symmetry with Sn—Sn = 2.707 (1), Sn—O(av) = 2.332 (3), C—O(av) = 1.23 (1), Sn—C = 2.10 (1) and C—C = 1.536 (9) Å. The fluorine atoms are disordered. The molecule possesses almost *mmm* symmetry, deviations from this being entirely attributable to a weak intermolecular C—H...O interaction.

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**Introduction.**  $\text{Sn}_2(\text{CH}_3)_4(\text{OOCF}_3)_2$  was prepared by the solvolysis of hexmethyltin with a tenfold excess of trifluoroacetic acid at 263 to 273 K. After gas evolution had ceased the mixture was filtered and the crystals were washed with fresh acid at 273 K. The crystals were dried and all manipulations were carried out under vacuum.

A cylindrically-shaped crystal 0.15 mm in diameter and 0.25 mm long, elongated along [312], was mounted on a Syntex  $P2_1$  diffractometer. Lattice parameters were calculated from the settings of 15 well centered reflections with  $18 \leq 2\theta \leq 31^\circ$  with Mo  $K\alpha$  radiation ( $\lambda = 0.71069 \text{ \AA}$ ). The only systematic absences were  $hkl$ ,  $h + k = 2n + 1$ , indicating one of

the space groups  $C2$ ,  $Cm$  or  $C2/m$ . The last was assumed and found to give satisfactory refinement. Intensities of 1182 reflections with  $2\theta < 55^\circ$  were measured using a  $\theta/2\theta$  scan. No correction was made for absorption ( $\mu r \sim 0.23$ ). Standard reflections measured at regular intervals showed no systematic variation. Equivalent reflections were averaged to give 1027 unique reflections out of a possible 1108 (the  $0kl$  and  $0k\bar{l}$  reflections were not averaged). Of these, 348 had intensities less than three times the standard counting error. The crystals were assumed to be isostructural with  $\text{Sn}_2(\text{CH}_3)_4(\text{OOCCH}_2\text{Cl})_2$  (Faggiani, Johnson, Brown & Birchall, 1978) and the positional and anisotropic temperature factors of the non-hydrogen atoms were refined by least-squares calculations with the locally-written program *CUDLS*. When the agreement index reached 0.09, a difference electron density map indicated disorder in the F positions. Two sets of half-weight F atoms were then refined. At  $R_w = 0.047$  a further difference map showed the positions of the methyl hydrogens whose positional (but not temperature,  $U = 0.08 \text{ \AA}^2$ ) parameters were refined. In the final cycle all parameters except the F and H temperature factors were varied to give  $R = 0.054$  and  $R_w = \{[\sum w(|F_o| - |F_c|)^2] / \sum w|F_o|^2\}^{1/2} = 0.042$  where  $w = [\sigma^2 + (0.023 F_o)^2]^{-1}$ ,  $\sigma$  being the standard error in  $F_o$  derived from counting statistics. The maximum value of shift over error was 1.5 for  $z(\text{H}3)$  (average value = 0.15). No extinction correction was made. Atomic scattering factors corrected for anomalous dispersion were taken from *International*

Table 1. Positional coordinates  $\times 10^4$  ( $\times 10^3$  for H) with standard errors in parentheses

All F positions have occupancy of 0.5.

	x	y	z
Sn	4477 (1)	0	1055 (1)
O(1)	6968 (4)	0	2124 (8)
O(2)	6118 (4)	0	3897 (7)
C(1)	6898 (6)	0	3673 (12)
C(2)	7916 (6)	0	5674 (12)
C(3)	4057 (6)	2186 (12)	1900 (11)
F(1)	8036 (6)	1254 (9)	6723 (11)
F(2)	8448 (8)	1257 (14)	5825 (20)
F(3)	8730 (8)	0	5370 (18)
F(4)	7803 (10)	0	7308 (18)
H(1)	464 (6)	289 (11)	267 (13)
H(2)	371 (6)	289 (11)	87 (12)
H(3)	394 (7)	200 (13)	251 (14)

Table 2. Interatomic distances ( $\text{\AA}$ ) and angles ( $^\circ$ )

Sn-Sn'	2.707 (1)	C(3)-Sn-C(3)	117.8 (4)
Sn-O(1)	2.319 (5)	C(3)-Sn-Sn'	121.1 (3) $\times 2$
Sn-O(2)	2.345 (4)	C(3)-Sn-O(1)	92.8 (2) $\times 2$
Sn-C(3)	2.100 (10) $\times 2$	C(3)-Sn-O(2)	93.2 (2) $\times 2$
		Sn-Sn-O(1)	84.6 (2)
		Sn-Sn-O(2)	83.8 (2)
		Sn-O(1)-C(1)	121.4 (5)
		Sn-O(2)-C(1)	120.3 (5)
C(1)-O(1)	1.218 (12)	O(1)-C(1)-O(2)	129.9 (6)
C(1)-O(2)	1.251 (12)	O(1)-C(1)-C(2)	115.9 (8)
C(1)-C(2)	1.536 (9)	O(2)-C(1)-C(2)	114.2 (8)
C(2)-F(1)	1.258 (9) $\times 2$	C(1)-C(2)-F(1)	112.9 (5) $\times 2$
C(2)-F(2)	1.274 (13) $\times 2$	C(1)-C(2)-F(2)	111.4 (7) $\times 2$
C(2)-F(3)	1.337 (18)	C(1)-C(2)-F(3)	112.4 (9)
C(2)-F(4)	1.318 (19)	C(1)-C(2)-F(4)	113.8 (9)
		F(1)-C(2)-F(1)'	110.2 (9)
C(3)-H(1)	0.97 (7)	F(1)-C(2)-F(3)	103.9 (7) $\times 2$
C(3)-H(2)	0.90 (8)	F(2)-C(2)-F(2)'	108.5 (10)
C(3)-H(3)	0.59 (13)	F(2)-C(2)-F(4)	105.7 (9) $\times 2$
H(1)...F(2)	2.60 (8)	Sn-C(3)-H(1)	112 (6)
H(1)...F(3)	2.76 (8)	Sn-C(3)-H(2)	115 (6)
H(2)...F(1)	2.87 (9)	Sn-C(3)-H(3)	105 (10)
H(2)...F(4)	2.92 (8)	H(1)-C(3)-H(2)	96 (7)
H(3)...F(4)	3.13 (12)	H(1)-C(3)-H(3)	102 (10)
H(3)...O(2)	3.20 (12)	H(2)-C(3)-H(3)	124 (11)

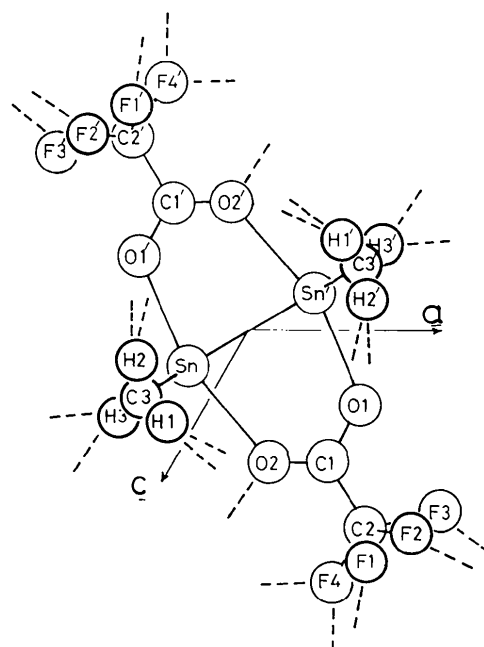


Fig. 1. Structure of  $\text{Sn}_2(\text{CH}_3)_4(\text{OOCF}_3)_2$ . All the F positions shown are half occupied. The molecule whose coordinates are given in Table 1 is centered at  $\frac{1}{2}, 0, 0$ . The dashed lines indicate the intermolecular  $\text{CH}\cdots\text{F}$  and  $\text{CH}\cdots\text{O}$  interactions.

*Tables for X-ray Crystallography* (1962). The final value of  $[\sum w(|F_o| - |F_c|)^2 / (N_F - N_p)]^{1/2} = 0.96$  where  $N_F$  = number of reflections and  $N_p$  = number of refined parameters. This indicates that the model accounts for all structurally significant information in the observed structure factors. The final coordinates are given in Table 1.\*

**Discussion.** Bond lengths and angles are given in Table 2 and the molecule is shown in Fig. 1. The dimeric molecule possesses crystallographic  $C_{2h}$  ( $2/m$ ) symmetry but is close to having  $D_{2h}$  ( $mmm$ ) symmetry. The temperature factors indicate that the whole molecule is librating around the long molecular axis with an

\* Lists of structure factors, anisotropic thermal parameters and bond valencies have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34241 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

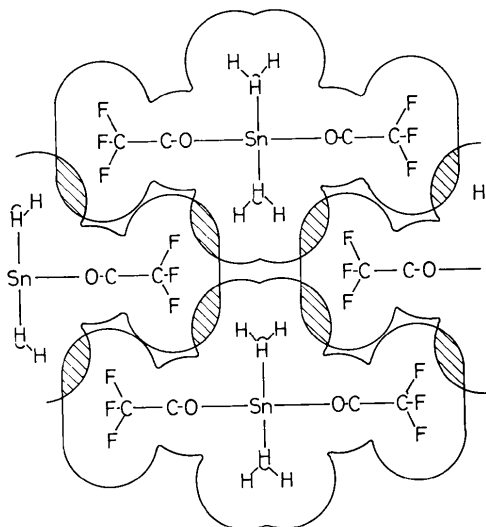


Fig. 2. Projection of molecules onto the  $(20\bar{1})$  plane showing the packing. Non-bonding radii shown for F = 1.5 Å, for O and H = 1.6 Å.

amplitude of about  $5^\circ$ . Although the hydrogen atom positions are well defined, the  $-\text{CF}_3$  groups are either disordered or rotating. The six half fluorine atoms included in the refinement have temperature factors that indicate an easy rotation. Bond valences calculated with only the intramolecular bond lengths give generally satisfactory valences for the individual atoms (Brown & Shannon, 1973) except for O(2) (atomic valence = 1.84) which forms significantly longer bonds than O(1) with Sn and possibly also with C(1). The interbond angles of the carboxyl group vary in a way which confirms that the bonding at O(2) is weaker, an effect that is attributable to an interaction between O(2) and two H(3) atoms in the molecule related by the  $(0,0,1)$  translation. These hydrogen atoms also bond to F(4). H(1) and H(2) interact with the fluorine atoms in the molecules related by the translations  $(\frac{1}{2}, \frac{1}{2}, 1)$  and  $(-\frac{1}{2}, \frac{1}{2}, -1)$ . In the  $(201)$  plane the molecules form a layer in which they key into each other like bricks in a wall (Fig. 2) with the  $\text{C}-\text{H}\cdots\text{F}$  interaction providing the cement. The ill-defined positions of the F atoms arise from the fact that the three F atoms of the  $-\text{CF}_3$  group interact with four H atoms of methyl groups in neighboring molecules. Although the weak  $\text{C}-\text{H}\cdots\text{O}$  and  $\text{C}-\text{H}\cdots\text{F}$  bonds individually have valences of around 0.03 units their inclusion in the bonding model decreases the standard deviation between the observed and expected atomic valences from 0.11 to 0.09 valence units. A table of the bond valencies has been included in the deposited material (see footnote).

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