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THE CRYSTAL AND MOLECULAR STRUCTURE OF TRIPHENYL(TRIFLUOROACETATO)GERMANIUM(IV)

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Summary

Crystals of the compound $Ph_3GeOCOCF_3$ are triclinic, space group $P\bar{1}$, with a 9.704(5), b 9.747(2), c 10.792(4) Å, α 73.30(3), β 86.68(3), γ 75.59(3)°, and $Z = 2$. The structure consists of monomeric molecules, with the geometry around germanium distorted towards trigonal bipyramidal by an intramolecular $Ge \cdots O$ interaction. There is no intermolecular association.

Introduction

We have recently reported the structures of a number of Group IV oxo-compounds containing R_3MO fragments, where R = Ph or $PhCH_2$: these include ethers $(R_3M)_2O$ [1–7], hydroxides [8], and a peroxide [9], and we now turn our attention to esters. The structures of a number of carboxylic esters containing Group IV elements have been reported [10–18], all derivatives of silicon or tin, but in the solid state most of them are associated [10–13, 16–18] with the carboxylate group acting as a bidentate ligand. When the Group IV element is fully substituted with phenyl groups, associated is eliminated in ethers [1–4], although not in hydroxides. Few, if any, esters of germanium have been structurally characterised, and here we report the crystal and molecular structure of triphenyl(trifluoroacetato)germanium(IV), $Ph_3GeOCOCF_3$.

Experimental

Triphenyl(trifluoroacetato)germanium(IV), $Ph_3GeOCOCF_3$, was prepared from Ph_4Ge and trifluoroacetic acid [19]. Crystals suitable for X-ray examination were grown from benzene solution.

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Data collection

Data were collected using a Stoe Stadi-2 two circle automatic diffractometer with graphite-crystal monochromatised Mo-K_α radiation for two crystals mounted about a. The intensities of 2491 independent reflections in the hemisphere $+h$ $\pm k$ $\pm l$ with $5 \leqslant 2\theta \leqslant 60°$, $h = 0$–12 $(0 \leqslant \mu \leqslant 26.067°)$ were measured using ω-2θ scan mode: layers 0–7 using one crystal and layer 8–12 (plus ca. 400 reflections from the lower layers for scaling purposes) using the second crystal. Throughout the data collection standard reflections were measured every 50 reflections and showed only small random deviations from their mean values. Lorentz and polarisation corrections

TABLE I

ATOM FRACTIONAL COORDINATES ($\times 10^3$, $\times 10^4$ FOR Ge) AND THE EQUIVALENT ISOTROPIC TEMPERATURE PARAMETERS (U_{eq})^{a,b}(Å^2, $\times 10^3$)

Atom	x	y	z	U_{eq}
Ge	1411(2)	4165(2)	2929(2)	48(1)
F(1a)	542(4)	176(6)	55(4)	89(12)
F(2a)	431(5)	351(4)	−50(4)	74(11)
F(3a)	336(7)	187(8)	−31(5)	101(15)
F(1b)	469(7)	124(5)	18(6)	86(14)
F(2b)	507(9)	303(10)	−7(7)	143(26)
F(3b)	332(5)	293(6)	−76(4)	64(11)
F(1c)	514(6)	119(6)	85(6)	39(14)
F(2c)	468(8)	367(7)	2(6)	54(17)
F(3c)	262(9)	252(9)	−48(7)	71(22)
F(1d)	389(9)	117(6)	−15(6)	48(16)
F(2d)	414(9)	78(8)	101(8)	99(27)
F(3d)	345(7)	364(6)	−84(5)	39(15)
O(1)	244(2)	375(1)	151(1)	74(9)
O(2)	301(2)	133(2)	224(2)	117(14)
C(1)	315(2)	258(3)	143(2)	83(15)
C(2)	396(3)	241(2)	31(2)	78(14)
C(11)	270(2)	336(1)	437(1)	50(9)
C(12)	312(2)	433(2)	497(2)	58(10)
C(13)	403(2)	376(2)	605(2)	75(13)
C(14)	455(2)	227(2)	655(2)	74(12)
C(15)	415(2)	130(2)	598(2)	75(12)
C(16)	325(2)	183(2)	492(2)	61(10)
C(21)	−19(2)	329(2)	304(2)	60(11)
C(22)	−53(2)	240(2)	425(2)	71(13)
C(23)	−177(3)	189(2)	439(3)	93(18)
C(24)	−270(3)	225(2)	331(3)	100(20)
C(25)	−230(3)	314(3)	206(3)	107(22)
C(26)	−105(3)	362(2)	199(2)	90(17)
C(31)	97(2)	635(2)	232(1)	58(9)
C(32)	210(2)	701(2)	187(2)	70(12)
C(33)	173(2)	853(2)	153(2)	74(13)
C(34)	37(3)	937(2)	167(2)	76(13)
C(35)	−69(2)	866(2)	210(2)	71(13)
C(36)	−43(2)	709(2)	245(2)	65(11)

[a] U_{eq} is defined as the geometric mean of the diagonal components of the diagonalised matrix of U_{ij}.
[b] Isotropic temperature parameters for F atoms. The site occupation factors for F(na) & F(nb) = 0.32(3) and for F(nc) & F(nd) = 0.18(3); (n = 1–3).

were applied to the data but no corrections for absorption were made. The data from the two crystals were scaled together using the intensities of ca. 400 common reflections.

Crystal data

Triphenyl(trifluoroacetato)germanium(IV), $C_{20}H_{15}F_3GeO_2$, $M_R = 416.92$. Triclinic, space group $P\bar{1}(C_i^1$, No.2). *a* 9.704(5), *b* 9.747(2), *c* 10.792(4) Å, α 73.30(3), β 86.68(3), γ 75.59(3)°; *U* 946.87 Å^3; $Z = 2$; D_c 1.462 kg dm^{-3}; $F(000) = 420$. Mo-K_α radiation, λ 0.71069 Å, μ(Mo-K_α) 1.584 mm^{-1}.

Structure solution and refinement

These were carried out using SHELX-76 [20]. The Ge position was obtained from a Patterson synthesis and the rest of the non-H atom positions were obtained from subsequent Fourier syntheses. The distribution of electron density around C(2) showed the F atoms to be disordered. In the initial stages of refinement two groups of three F atom positions were used with the site occupation factors (s.o.f.) for each group allowed to vary, but constrained so that the two s.o.f.'s summed to 1: these refined to be equal within experimental error. Residual electron density around C(2) furnished six more F atom partial positions. These were included in the refinement: s.o.f.'s were varied for this group and the initial group of 6 positions such that the two s.o.f.'s were constrained to sum to 0.5. The structure was refined using 2112

TABLE 2

ANISOTROPIC TEMPERATURE PARAMETERS (Å^2, $\times 10^3$)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ge	75(1)	32(1)	52(1)	−13(1)	4(1)	−8(1)
O(1)	182(14)	49(6)	56(7)	−17(5)	−5(8)	26(7)
O(2)	212(19)	75(9)	113(12)	−26(9)	9(12)	−18(10)
C(1)	93(16)	107(16)	69(12)	−24(11)	6(11)	27(13)
C(2)	118(18)	75(12)	82(12)	−44(11)	−13(13)	8(12)
C(11)	69(10)	39(7)	55(9)	−10(6)	20(7)	−5(7)
C(12)	76(11)	63(9)	55(10)	−18(8)	−3(9)	−26(8)
C(13)	95(14)	77(12)	72(12)	−23(10)	9(11)	−26(10)
C(14)	84(13)	90(13)	56(11)	−2(10)	−7(10)	−11(11)
C(15)	89(14)	73(11)	67(11)	−4(9)	−2(10)	−16(10)
C(16)	91(13)	39(8)	63(10)	−2(7)	−10(10)	1(8)
C(21)	87(13)	43(8)	85(12)	−34(8)	−3(10)	−8(8)
C(22)	110(16)	43(9)	103(14)	−20(9)	19(12)	−31(9)
C(23)	133(22)	58(11)	140(12)	−24(12)	25(18)	−38(13)
C(24)	115(20)	69(13)	177(26)	−43(16)	7(19)	−36(13)
C(25)	131(23)	87(16)	196(29)	−56(18)	−34(21)	−42(15)
C(26)	171(24)	61(11)	109(17)	−21(11)	−52(17)	−30(13)
C(31)	78(12)	53(8)	51(9)	−11(7)	1(8)	−11(8)
C(32)	92(14)	45(8)	96(13)	−5(8)	−7(11)	−22(9)
C(33)	122(18)	43(9)	98(14)	−4(9)	−3(13)	−33(10)
C(34)	115(17)	51(10)	81(13)	−13(9)	13(12)	−11(11)
C(35)	123(18)	38(8)	85(13)	−11(8)	18(12)	8(10)
C(36)	102(14)	42(8)	68(11)	−9(7)	10(10)	7(8)

TABLE 3

BOND LENGTHS (Å)

Ge–O(1)	1.86(1)	Ge···O(2)	3.09(1)		
Ge–C(11)	1.91(2)	Ge–C(21)	1.93(2)	Ge–C(31)	1.98(1)
O(1)–C(1)	1.20(3)	O(2)–C(1)	1.32(3)	C(1)–C(2)	1.43(3)
C(2)–F, range: 1.22–1.56; mean: 1.39(12)					
Phenyl C–C, range: 1.36–1.44; mean: 1.40(3)					

reflections having $F_0 \geqslant 6\sigma\ (F_0)$ with the least-squares matrix blocked so that the $GeOCOCF_3$ and the Ph_3Ge groups refined in alternate cycles. With anisotropic temperature parameters for Ge, O and C atoms and isotropic temperature parameters for the partial F atoms and no H atoms included, the refinement converged to give a conventional R index $[=\Sigma\Delta/\Sigma F_0, (\Delta = |F_0 - F_c|)]$ of 0.1168 and a generalised index $R_G[=(\Sigma w\Delta^2/\Sigma wF_0^2)^{1/2}]$ of 0.1267. In the final cycles of refinement 257 parameters were varied comprising 105 positional parameters, 138 anisotropic temperature components, 12 isotropic temperature parameters, 1 independent s.o.f. and 1 overall scale factor. A final difference synthesis showed no significant residual features. The reductions in R_G at all stages of the refinement were significant at the 99.5% level [21]. Complex neutral-atom scattering factors [22,23] were employed for all atoms. The results of the final least-squares cycles are given in Tables 1 and 2. These, together with the covariance matrix were used to calculate the bond lengths and angles and torsion angle which are given with e.s.d.'s in Tables 3 and 4. Figure 1 is a perspective view of the molecule showing the atom numbering scheme. Figure 2 shows the unit cell. Tables of calculated and observed structure factors are available (from C.G.) on request.

Results and discussion

The structure consists of isolated molecules. The Ge–O distance, 1.86 Å is rather longer than those found in $(Ph_3Ge)_2O$ [1] and $[(PhCH_2)_3Ge]_2O$ [6], 1.767 and 1.730 Å, respectively: the GeOC angle, 128.2° is very wide in comparison with the analogous angles in other monomeric Group IV esters [14,15], and the Ge···C distance spanned by this angle is 2.77 Å, very close to the limiting contact distance for germanium and carbon separated by one angle [24]. The conformation of the GeOCO chain is approximate *cis*, as usual in esters but the heavy atom skeleton is not exactly planar: the dihedral angle GeOCO is 17.6° and the dihedral angle GeOCC is −176.3°; similar non-planarity has been observed in the thio-ester $H_3SiOC(S)CH_3$[18], where the dihedral angles SiOCS and SiOCC are 6.0° and −174.8° respectively.

Within the Ph_3GeO group, the bond angles around germanium are somewhat distorted from tetrahedral. The C–Ge–C angles range from 112.9(7) to 115.9(7)° (see Table 4), while of the remaining angles, O–Ge–C(31), is 98.9(6)°, and the other two O–Ge–C(11) and O–Ge–C(21) are closely similar, 106.2(6) and 105.1(8)°. The very low-valued angle O–Ge–C(31) is the O–Ge–C angle which lies closest to the plane of the GeOCO plane and we take this, together with the larger than tetrahedral angles C–Ge–C as indicative of a weak intramolecular interaction

TABLE 4

SELECTED BOND ANGLES AND TORSION ANGLES [a] (°)

Bond angles			
O(1)–Ge–C(11)	106.2(6)	O(1)–Ge–C(21)	105.1(8)
O(1)–Ge–C(31)	98.9(6)	C(11)–Ge–C(21)	115.5(7)
C(11)–Ge–C(31)	112.9(7)	C(21)–Ge–C(31)	115.9(7)
Ge–O(1)–C(1)	128.2(11)	O(1)–C(1)–O(2)	122(2)
O(1)–C(1)–C(2)	123(2)	O(2)–C(1)–C(2)	114(2)
Torsion angles			
Ge–O(1)–C(1)–O(2)	17.6(9)	Ge–O(1)–C(1)–C(2)	−176.3(16)
C(1)–O(1)–Ge–C(11)	51.5(15)	C(1)–O(1)–Ge–C(21)	−71.3(16)
C(1)–O(1)–Ge–C(31)	168.6(18)		

[a] The torsion angle *i-j-k-l* is positive if, when viewed in the direction *j* → *k*, the projection of *i-j* has to be rotated clockwise to coincide with the projection of *k-l*.

Ge $\cdots$ O(2). For comparison the mean values of the O–Ge–C and C–Ge–C angles in $(Ph_3Ge)_2O$ are [1] 107.6 and 111.2°, respectively. The distance Ge $\cdots$ O(2) is 3.09(1) Å, considerably shorter than the sum, approximately 3.50 Å, of the Van der Waals radii of germanium and oxygen [25]. Further supportive evidence for the existence of such a Ge $\cdots$ O interaction is found in the Ge–C distances: whereas in $(Ph_3Ge)_2O$ the mean Ge–C distance is 1.942(3) Å [1], in $Ph_3GeOCOCF_3$, the distance to C(31) i.e. that *trans* to the Ge $\cdots$ O interaction is 1.98(1) Å while the other two are 1.91(2) and 1.93(2) Å. Overall the geometry about the germanium may

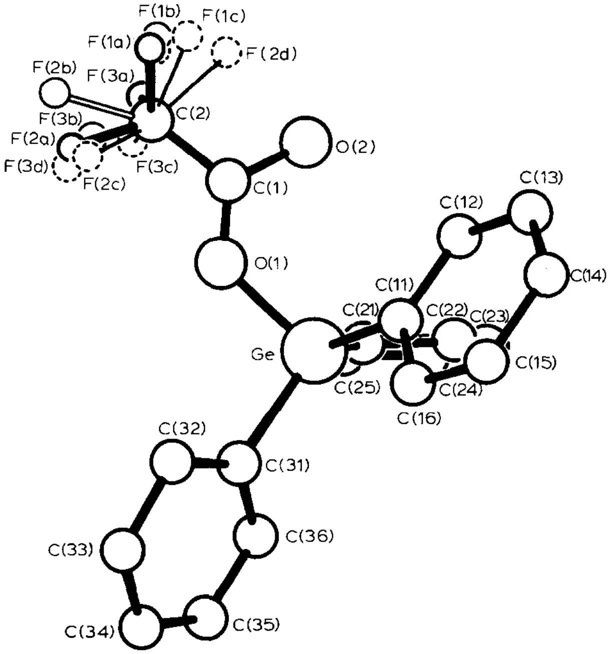

Fig. 1. A perspective view of the molecule showing the atom numbering scheme.

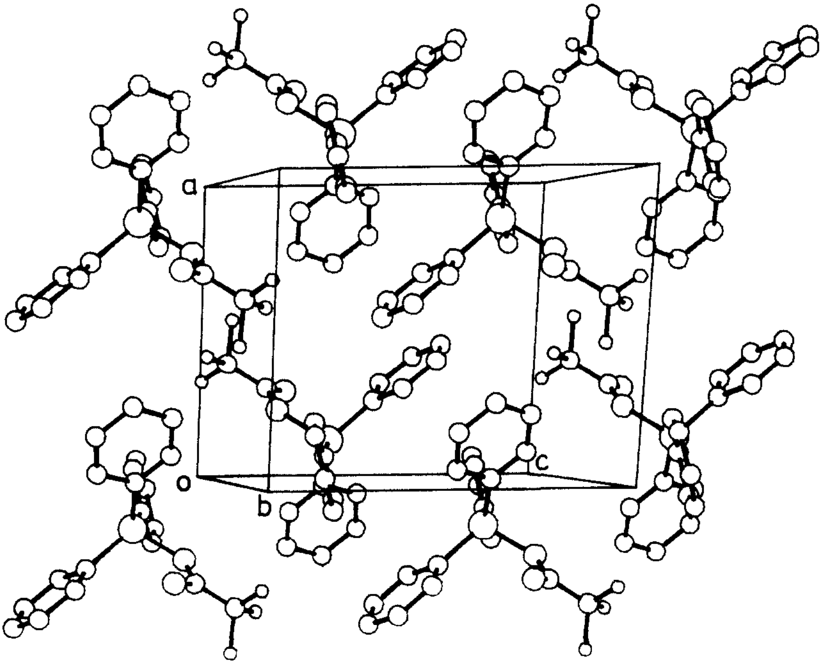

Fig. 2. A perspective view of the unit cell viewed perpendicular to the B face: all molecules whose centres are in the range 0 to 1 in y and -0.5 to $+1.5$ in x and z are shown.

be regarded as a distortion of tetrahedral towards trigonal bipyramidal with C(11), C(21) and O(1) occupying the equatorial sites and C(31) and O(2) occupying the axial sites (see Fig. 1). In contrast, the shortest intermolecular Ge · · · O distances are Ge · · · O(1)^{i} of 5.80(2) and Ge · · · O(2)^{i} of 6.89(2) Å (the superscript i indicates the symmetry position $-x$, $1-y$, $-z$): the complete absence of intermolecular association is clearly shown by the view of the unit-cell contents in Fig. 2.

Within the trifluoroacetato group, the three fluorine atoms are heavily disordered: the best representation determined from the X-ray data comprises twelve partially occupied sites, one set of six with s.o.f. 0.32(3) and a second set with s.o.f. 0.18(3). This model is indicative of a very high amplitude librational motion of the CF_3 group, which almost approximates to free rotation about the C–C bond.

References

1 C. Glidewell and D.C. Liles, Acta Cryst., B, 34 (1978) 119.
2 G. Glidewell and D.C. Liles, Acta Cryst., B, 34 (1978) 124.
3 C. Glidewell and D.C. Liles, Acta Cryst., B, 34 (1978) 696.
4 C. Glidewell and D.C. Liles, Acta Cryst., B, 34 (1978) 1693.
5 C. Glidewell and D.C. Liles, Acta Cryst., B, 35 (1979) 1689.
6 C. Glidewell and D.C. Liles, J. Organometal. Chem., 174 (1979) 275.
7 C. Glidewell and D.C. Liles, J. Organometal. Chem., 212 (1981) 291.
8 C. Glidewell and D.C. Liles, Acta Cryst., B. 34 (1978) 129.
9 C. Glidewell, D.C. Liles, D.J. Walton and G.M. Sheldrick, Acta Cryst., B, 35 (1979) 500.

10 G.M. Sheldrick and R. Taylor, Acta Cryst., B, 31(1975) 2740.

11 H. Chih and B.R. Penfold, J. Cryst. Mol. Structure, 3 (1973) 285.

12 S. Calogero, D.A. Clemente, V. Peruzzo and G. Tagliarini, J. Chem. Soc. Dalton, (1979) 1172.

13 N.W. Alcock and R.E. Timms, J. Chem. Soc. (A), (1968) 1873.

14 N.W. Alcock and R.E. Timms, J. Chem. Soc. (A), (1968) 1876.

15 S. Calogero, P. Ganis, V. Peruzzo, and G. Tagliarini, J. Organometal. Chem., 191 (1980) 381.

16 M.J. Barrow, S. Cradock, E.A.V. Ebsworth and D.W.H. Rankin, J. Chem. Soc. Dalton, (1981) 1988.

17 B. Kamenar and M. Bruvo, Z. Krist., 141 (1975) 97.

18 M.J. Barrow, E.A.V. Ebsworth, C.M. Huntley and D.W.H. Rankin, J. Chem. Soc. Dalton, (1982) 1131.

19 P. Sartori and M. Weidenbruch, Angew. Chem. Int. Ed., 4 (1965) 1079; Chem. Ber., 100 (1967) 2049.

20 G.M. Sheldrick, SHELX-76 program system, University of Cambridge, 1976.

21 W.C. Hamilton, Acta Cryst., 18 (1965) 502.

22 D.T. Cromer and J.B. Mann, Acta Cryst., A, 24 (1968) 321.

23 P.A. Doyle and P.S. Turner, Acta Cryst., A, 24 (1968) 390.

24 C. Glidewell, Inorg. Chim. Acta, 12 (1975) 219.

25 A. Bondi, J. Phys. Chem., 68 (1964) 441.