# Novel Terdentate Hydrated β-Diketone Complexes of Triarylantimony(v)

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*Summary* Novel complexes of fluorinated β-diketone hydrate with triarylantimony(v), $Ar_3Sb[CF_3C(O)_2CH_2COR]$ (Ar=Ph or $p$-$ClC_6H_4$, and R=Me or Ph), have been synthesized, in which the ligand acts as a terdentate ligand co-ordinated to the central antimony atom by a pair of *gem*-diol oxygen atoms as well as the carbonyl oxygen.

We have found that triarylantimony(v) forms complexes with 1,1,1-trifluoropentane-2,4-dione (Htfac), and 4,4,4-trifluoro-1-phenylbutane-1,3-dione (Htfbz), in which a pair of diolato oxygen atoms and a carbonyl oxygen are co-ordinated to the central antimony atom. The complexes are formulated as $Ar_3Sb[CF_3C(O)_2CH_2COR]$, where Ar=Ph or $p$-$ClC_6H_4$, and R=Me or Ph.

When dibromotriphenylantimony(v),[1] a β-diketone, and triethylamine (deprotonation reagent) were mixed in dried benzene the oxygen-bridged enol-type β-diketone complex, $[Ar_3SbL]_2O$ (where Ar=Ph or $p$-$ClC_6H_4$, and HL=β-diketone) was obtained by a metathetical reaction.[2] When complexes of this type using fluorinated β-diketones were boiled for several hours or allowed to stand for a few days at room temperature in a moist organic solvent, *e.g.* acetonitrile, the title complexes were obtained. They were recrystallized from a mixture of dried dichloroethane and light petroleum, or dried acetonitrile. Although enol-type complexes of pentane-2,4-dione, and 1-phenylbutane-1,3-dione were obtained, complexes of this new type have not been isolated yet.

An *X*-ray crystal and molecular analysis of the tris($p$-chlorophenyl)antimony(v) complex of hydrated Htfac, $(p\text{-}ClC_6H_4)_3Sb[CF_3C(O)_2CH_2COMe]$, was carried out. The crystals are monoclinic, space group $P2_1/c$, $a = 11{\cdot}518(1)$, $b = 20{\cdot}962(2)$, $c = 12{\cdot}259(1)$ Å; $\beta = 124{\cdot}081(7)°$; $U = 2451{\cdot}57$ Å$^3$; $D_c = 1{\cdot}70$, $D_m = 1{\cdot}68$ g cm$^{-3}$, $Z = 4$. Intensity data were collected by the $\omega - 2\theta$ scan method ($2\theta < 50°$) on a Rigaku automated four circle diffractometer using Mo-$K_\alpha$ radiation (0·71069 Å). The crystal was stable in air and used uncovered. Of the 4518 independent reflections, 2784 [$I > 3\sigma(I)$] were used in the calculations. The positions of the antimony atoms were deduced from a

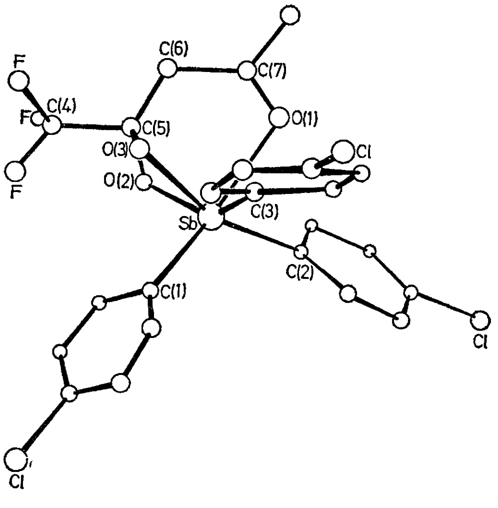

Figure. Molecular structure of $(p\text{-}ClC_6H_4)_3Sb[CF_3C(O)_2CH_2COMe]$. Bond lengths(Å): mean Sb–C(1,2,3) 2·12(1); mean Sb–O(2,3) 2·03(1); Sb–O(1) 2·52(1); mean C(5)–O(2,3) 1·45(2); C(7)–O(1) 1·23(2); bond angles (°): C(1)–Sb–C(2) 100·3(4); C(1)–Sb–C(3) 103·9(5); C(1)–Sb–O(2) 97·4(5); C(1)–Sb–O(3) 102·9(4); C(2)–Sb–O(1) 80·9(3); C(2)–Sb–O(2) 93·0(5); C(3)–Sb–O(1) 81·7(4); C(3)–Sb–O(3) 88·7(4); mean O(1)–Sb–O(2,3) 71·3(3); O(2)–Sb–O(3) 67·4(4).

TABLE. $^1H$ and $^{19}F$ n.m.r. spectral data (in p.p.m., $^1H$ ref. $Me_4Si$, $^{19}F$ ref. 1,1,2,2-tetrachloro-3,3,4,4-tetrafluorocyclobutane).

| | Aryl | | Ligand | | | | $^{19}F$- n.m.r. |
|---|---|---|---|---|---|---|---|
| Compounds | *o*- | *m*-, *p*- | –CH= | –$CH_2$– | Me | Ph | |
| Htfac | | | 5·90 | | 2·19 | | 45·1[a] |
| $Ph_3Sb(HLO)$ | 7·68 | 7·46 | | 3·16 | 2·22 | | 37·3[a] |
| $[Ph_3SbL]_2O$ | 7·52 | 7·24 | 5·36 | | 1·90 | | 46·7[a] |
| $(p\text{-}Cl{\cdot}C_6H_4)_3Sb(HLO)$ | 7·49[c] | 7·33[c] | | 3·06 | 2·14 | | |
| $[(p\text{-}Cl{\cdot}C_6H_4)_3SbL]_2O$ | 7·35[c] | 7·03[c] | 5·46 | | 1·97 | | |
| Htfbz | | | 6·45 | | 7·87 | 7·50 | 44·5[b] |
| $Ph_3Sb(HLO)$ | 7·65 | 7·36 | | 3·45 | 7·65 | 7·36 | 37·2[b] |
| $[Ph_3SbL]_2O$ | 7·55 | 7·30 | 6·01 | | 7·15 | 7·05 | 46·2[b] |

[a] benzene, [b] $CHCl_3$, in all other cases $CDCl_3$ solutions were used, [c] AB pattern, *J* 8 Hz.

three dimensional Patterson map, and the remaining non-hydrogen atoms were located in the subsequent Fourier maps. The structure has been refined by block-diagonal least squares to $R = 0{\cdot}067$, The projection of the molecule along the *c*-axis is shown in the Figure.

The co-ordination around the antimony atom is deformed octahedral with three aryl groups in facial positions. Although the distance between antimony and the carbonyl oxygen atom, Sb–O(1), is longer than the usual Sb–O single bond, it is still considered to be in the bonding range. The arrangement of two oxygen and two carbon atoms around C(5) is approximately tetrahedral. The distances between C(5)–C(6) and C(6)–C(7) of the β-diketone skeleton are typical of C–C single bonds.

The $^1H$ and $^{19}F$ n.m.r. spectral data of the complexes prepared and related compounds are shown in the Table. The enol-type complexes have a methine proton, while the title ones have methylene protons. The ν(C=O) band for complexes of the type $Ar_3Sb(HLO)$ is seen at 1683 (Ar=Ph, L=tfac), 1645 (Ar=Ph, L=tfbz), and 1682 $cm^{-1}$ (Ar=Cl-$C_6H_4$, L=tfac), while ν(C=O) for the enol-type dimer, $[Ar_3SbL]_2O$, is 1637, 1610, and 1634 $cm^{-1}$, respectively.

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[1] A. Reese, *Annalen*, 1886, **233**, 50; P. Pfeiffer, *Ber.*, 1904, **37**, 4620.

[2] A. Ouchi, H. Honda, and S. Kitazima, *J. Inorg. Nuclear Chem.*, 1975, **37**, 2559. The synthetic technique used is an extension of the one in this reference.