

Structure of $(R_f)_2(\text{Cl})\text{Sn}^{\text{IV}}(\mu_2\text{-O})\text{Sn}^{\text{IV}}(\text{Cl})(R_f)_2$; $R_f = 2,4,6\text{-Tris(trifluoromethyl)phenyl}$

BY S. BROOKER, F. T. EDELMANN AND D. STALKE

Institut für Anorganische Chemie der Universität Göttingen, Tammannstraße 4, D-3400 Göttingen, Germany

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Abstract. μ -Oxo-bis{chlorobis[2,4,6-tris(trifluoromethyl)phenyl]tin}, $\text{C}_{36}\text{H}_8\text{Cl}_2\text{F}_{36}\text{OSn}_2$, $M_r = 1448.7$, monoclinic, $P2_1/n$, $a = 15.100(1)$, $b = 14.830(1)$, $c = 20.169(2)$ Å, $\beta = 95.18(1)^\circ$, $V = 4498.1(6)$ Å³, $Z = 4$, $D_x = 2.14$ g cm⁻³, $\lambda(\text{Mo K}\alpha) = 0.71069$ Å, $\mu = 14.1$ cm⁻¹, $F(000) = 2760$, $T = 153$ K, $R = 0.039$ for 6140 observed reflections. This dimeric compound is an oxidation product of $\text{Sn}^{\text{II}}(R_f)_2$. The two $\text{Sn}^{\text{IV}}(\text{Cl})(R_f)_2$ groups are bridged by a μ_2 -oxo moiety [$\text{Sn}(1)\text{—O}(1)\text{—Sn}(2) = 144.8(2)^\circ$]. The geometry at the Sn atoms is distorted tetrahedral. Average bond lengths to the Sn atoms are as follows: Sn—O 1.937(3), Sn—Cl 2.315(1) and Sn—C 2.194(5) Å.

Introduction. In recent years the 2,4,6-tris(trifluoromethyl)phenyl substituent (R_f) has become a highly versatile building block in main-group chemistry (Carr, Chambers, Holmes & Parker, 1987; Scholz, Roesky, Stalke, Keller & Edelmann, 1989). Due to its combination of sterically and electronically stabilizing effects the R_f ligand allows the isolation of main-group compounds with unusually low coordination numbers. Among these are the stable diaryl stannylene $\text{Sn}(R_f)_2$ (Grützmaier, Pritzkow & Edelmann, 1991) and the first example of a stable diaryl lead compound, $\text{Pb}(R_f)_2$ (Brooker, Buijink & Edelmann, 1991). Crystals of the title compound $(R_f)_2(\text{Cl})\text{Sn}^{\text{IV}}(\mu_2\text{-O})\text{Sn}^{\text{IV}}(\text{Cl})(R_f)_2$ (1) were isolated from an unsuccessful attempt to prepare $\text{Sn}(R_f)_2$. The formation of (1) can be explained as an air oxidation of the original reaction mixture containing $\text{Sn}^{\text{II}}(R_f)_2$ and Cl^- .

Experimental. An attempted crystallization of $\text{Sn}(R_f)_2$ from a hexane reaction solution (Grützmaier, Pritzkow & Edelmann, 1991) yielded colourless crystals of $(R_f)_2(\text{Cl})\text{Sn}^{\text{IV}}(\mu_2\text{-O})\text{Sn}^{\text{IV}}(\text{Cl})(R_f)_2$ (1). A block approximate $0.5 \times 0.5 \times 0.5$ mm was used for data collection at 153 K on a Siemens-Stoe AED four-circle diffractometer. Lattice parameters were refined from 70 reflections with $20 < 2\theta < 25^\circ$. 2θ - ω scans, with online profile fitting (Clegg, 1981) and variable scan speeds, were employed for data collection ($8 < 2\theta < 48^\circ$, index ranges $h \pm 17$, k

$0/16$, l $0/23$). There was no significant variation in the three standard reflections. 7028 reflections were measured of which all were unique, and 6140 observed [$F > 3.0\sigma(F)$]. A semi-empirical absorption correction was applied ($T_{\text{min}} 0.750$, $T_{\text{max}} 0.915$).

The structure was solved by Patterson methods (SHELXS86; Sheldrick, 1986) and refined by full-matrix least-squares (on F) techniques (modified SHELX76; Robinson & Sheldrick, 1988). All non-H atoms were refined anisotropically; H atoms were inserted at calculated positions with a common isotropic thermal parameter (0.036 Å²). Rotational disorder of two of the *para*-CF₃ groups was apparent. This was modelled by the insertion of a second component, and the F atoms 'opposite' each other were constrained to have identical U_{ij} values. $R = 0.039$, $wR = 0.047$, $g = 0.0006$, goodness-of-fit = 1.41, 714 parameters, $(\Delta/\sigma)_{\text{max}} = 0.002$, $\Delta\rho = +0.97/-0.90$ e Å⁻³, $w^{-1} = \sigma^2(F) + gF^2$. Scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV).

Discussion. Oxidation of $\text{Sn}^{\text{II}}(R_f)_2$ in the presence of Cl^- led to the formation of the μ_2 -oxo bridged dimeric species, $(R_f)_2(\text{Cl})\text{Sn}^{\text{IV}}(\mu_2\text{-O})\text{Sn}^{\text{IV}}(\text{Cl})(R_f)_2$, (1), which has been characterized by an X-ray crystal structure analysis. Final atom coordinates are listed in Table 1 and selected bond lengths and angles are given in Table 2.* Fig. 1 shows a partially labelled perspective view of (1). The two Sn atoms have distorted tetrahedral geometries; each is bound to two R_f moieties, one chloride and the μ_2 -oxo atom. The R_f groups are demanding both sterically and electronically. The C(1) and C(10) aromatic rings [bound to Sn(1)] have an angle of $85.4(3)^\circ$ between them, and the C(19) and C(28) aromatic rings [bound to Sn(2)] an angle of $74.7(3)^\circ$ between them.

* Lists of structure factors, complete bond length and angle tables, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54306 (22 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($\text{\AA}^2 \times 10^3$)

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{eq}
Sn(1)	2487.3 (2)	571.8 (2)	3830.9 (2)	30 (1)
Sn(2)	3885.2 (2)	1920.6 (2)	2793.3 (2)	30 (1)
O(1)	3453 (2)	1282 (2)	3540 (2)	34 (1)
Cl(1)	1654.8 (8)	153.0 (9)	2863.0 (6)	44 (1)
Cl(2)	2632.3 (8)	2260.5 (9)	2086.6 (7)	47 (1)
C(1)	2784 (3)	-775 (3)	4251 (2)	33 (1)
C(2)	3529 (3)	-1275 (3)	4094 (2)	30 (1)
C(3)	3704 (3)	-2137 (3)	4346 (2)	34 (1)
C(4)	3136 (3)	-2528 (3)	4762 (2)	35 (1)
C(5)	2390 (3)	-2074 (3)	4913 (3)	41 (2)
C(6)	2212 (3)	-1204 (3)	4659 (2)	37 (2)
C(7)	4161 (3)	-909 (3)	3627 (2)	37 (2)
F(1)	3719 (2)	-524 (2)	3093.4 (13)	39 (1)
F(2)	4696 (2)	-272 (2)	3918.8 (14)	46 (1)
F(3)	4685 (2)	-1541 (2)	3396 (2)	48 (1)
C(8)	3321 (4)	-3461 (3)	5026 (3)	44 (2)
F(4)†	4175 (4)	-3755 (5)	4963 (6)	86 (3)
F(5)†	2878 (8)	-4074 (4)	4720 (7)	122 (4)
F(6)†	3256 (10)	-3544 (4)	5658 (4)	103 (4)
F(37)†	3951 (19)	-3473 (8)	5430 (15)	122 (4)
F(38)†	2581 (10)	-3768 (11)	5289 (13)	86 (3)
F(39)†	3368 (19)	-4004 (12)	4551 (9)	103 (4)
C(9)	1393 (4)	-767 (4)	4872 (3)	48 (2)
F(7)	780 (2)	-1342 (2)	5026 (2)	78 (2)
F(8)	1569 (3)	-225 (3)	5398 (2)	82 (2)
F(9)	1006 (2)	-224 (2)	4399 (2)	60 (1)
C(10)	1966 (3)	1583 (3)	4484 (2)	34 (1)
C(11)	1201 (3)	2115 (3)	4318 (3)	38 (2)
C(12)	989 (3)	2840 (3)	4703 (3)	41 (2)
C(13)	1532 (3)	3067 (3)	5273 (3)	40 (2)
C(14)	2262 (3)	2555 (3)	5460 (3)	40 (2)
C(15)	2478 (3)	1823 (3)	5073 (2)	36 (2)
C(16)	603 (3)	1957 (4)	3691 (3)	49 (2)
F(10)	1032 (2)	2092 (2)	3148 (2)	64 (1)
F(11)	281 (2)	1110 (2)	3648 (2)	53 (1)
F(12)	-102 (2)	2491 (2)	3642 (2)	81 (2)
C(17)	1313 (4)	3883 (4)	5658 (3)	56 (2)
F(13)	488 (3)	4083 (4)	5609 (3)	153 (3)
F(14)	1569 (3)	3816 (3)	6295 (2)	96 (2)
F(15)	1719 (4)	4595 (3)	5472 (2)	118 (2)
C(18)	3294 (4)	1326 (3)	5357 (2)	43 (2)
F(16)	3956 (2)	1879 (2)	5554 (2)	65 (1)
F(17)	3625 (2)	761 (2)	4925 (2)	55 (1)
F(18)	3135 (3)	849 (3)	5886 (2)	80 (2)
C(19)	4437 (3)	3276 (3)	2984 (2)	33 (1)
C(20)	4243 (3)	3798 (3)	3527 (2)	35 (1)
C(21)	4638 (3)	4637 (3)	3661 (3)	41 (2)
C(22)	5240 (3)	4972 (3)	3247 (3)	44 (2)
C(23)	5426 (3)	4496 (3)	2697 (3)	41 (2)
C(24)	5030 (3)	3663 (3)	2560 (3)	35 (1)
C(25)	3580 (4)	3483 (3)	3989 (3)	46 (2)
F(19)	3934 (2)	2832 (2)	4401 (2)	55 (1)
F(20)	2854 (2)	3132 (2)	3666 (2)	48 (1)
F(21)	3307 (3)	4138 (2)	4375 (2)	75 (1)
C(26)	5656 (4)	5877 (4)	3393 (4)	60 (2)
F(22)†	5072 (4)	6532 (3)	3339 (8)	110 (4)
F(23)†	6027 (10)	5927 (6)	4012 (4)	129 (4)
F(24)†	6274 (7)	6094 (5)	3014 (6)	103 (3)
F(40)†	6448 (18)	5836 (15)	3548 (32)	110 (4)
F(41)†	5515 (39)	6408 (24)	2889 (16)	129 (4)
F(42)†	5349 (28)	6305 (21)	3888 (23)	103 (3)
C(27)	5262 (3)	3218 (3)	1937 (3)	46 (2)
F(25)	5445 (3)	3796 (2)	1471 (2)	76 (1)
F(26)	5963 (2)	2666 (3)	2042 (2)	72 (1)
F(27)	4609 (2)	2681 (2)	1661 (2)	59 (1)
C(28)	4872 (3)	944 (3)	2511 (2)	29 (1)
C(29)	5679 (3)	849 (3)	2907 (2)	33 (1)
C(30)	6300 (3)	198 (3)	2787 (2)	35 (1)
C(31)	6128 (3)	-409 (3)	2276 (3)	38 (2)
C(32)	5332 (3)	-352 (3)	1876 (2)	36 (2)
C(33)	4720 (3)	315 (3)	1991 (2)	31 (1)
C(34)	5957 (3)	1445 (3)	3499 (3)	42 (2)
F(28)	5265 (2)	1823 (2)	3767.1 (14)	48 (1)
F(29)	6461 (3)	2124 (3)	3343 (2)	85 (2)
F(30)	6394 (3)	993 (2)	3988 (2)	82 (1)
C(35)	6788 (4)	-1137 (4)	2168 (3)	58 (2)
F(31)	7585 (2)	-895 (3)	2297 (4)	170 (3)
F(32)	6705 (3)	-1448 (3)	1543 (2)	97 (2)
F(33)	6639 (3)	-1871 (3)	2506 (3)	112 (2)
C(36)	3879 (3)	336 (3)	1523 (2)	42 (2)

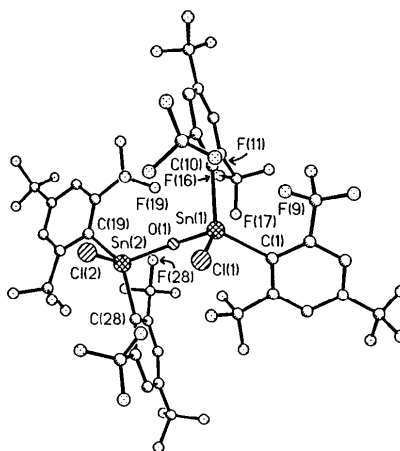
Table 1 (cont.)

	x	y	z	U_{eq}
F(34)	3837 (2)	-338 (2)	1087 (2)	62 (1)
F(35)	3156 (2)	279 (2)	1857.4 (14)	46 (1)
F(36)	3800 (2)	1103 (2)	1172.6 (14)	53 (1)

† Rotationally disordered *para*-CF₃ groups (see *Experimental*). Occupancies: F(4), F(5), F(6) 0.67; F(37), F(38), F(39) 0.33; F(22), F(23), F(24) 0.79; F(40), F(41), F(42) 0.21.

Table 2. Selected bond lengths (\AA) and angles ($^\circ$)

Sn(1)—O(1)	1.932 (3)	Sn(1)—Cl(1)	2.310 (1)
Sn(1)—C(1)	2.199 (4)	Sn(1)—C(10)	2.188 (5)
Sn(2)—O(1)	1.942 (3)	Sn(2)—Cl(2)	2.319 (1)
Sn(2)—C(19)	2.197 (4)	Sn(2)—C(28)	2.190 (4)
O(1)—Sn(1)—Cl(1)	105.0 (1)	O(1)—Sn(1)—C(1)	118.6 (1)
Cl(1)—Sn(1)—C(1)	99.1 (1)	O(1)—Sn(1)—C(10)	97.5 (2)
Cl(1)—Sn(1)—C(10)	119.7 (1)	C(1)—Sn(1)—C(10)	117.5 (2)
O(1)—Sn(2)—Cl(2)	105.7 (1)	O(1)—Sn(2)—C(19)	117.3 (2)
Cl(2)—Sn(2)—C(19)	100.6 (1)	O(1)—Sn(2)—C(28)	99.4 (1)
Cl(2)—Sn(2)—C(28)	121.4 (1)	C(19)—Sn(2)—C(28)	113.2 (2)
Sn(1)—O(1)—Sn(2)	144.8 (2)		

Fig. 1. Perspective view of $(R_f)_2(Cl)Sn^{IV}(\mu_2-O)Sn^{IV}(Cl)(R_f)_2$ (1), showing the principal CF₃ orientations.

Likewise, approximately 90° angles are observed between the rings in each of the following pairs: C(1), C(28) $88.5(3)^\circ$ and C(10), C(19) $97.8(3)^\circ$. Rings C(10) and C(28) are oriented almost parallel to each other [$172.2(3)^\circ$] but they are staggered about Sn(1)—O(1)—Sn(2) so are well separated in space. However, there are still numerous intra- and intermolecular F—F contacts of between 2.77 and 2.90 \AA . There are only two contacts shorter than this, F(9)⋯F(11) = 2.666 (8) and F(16)⋯F(19) = 2.719 (8) \AA , and these two distances are close to the sum of the van der Waals radii of F atoms (approx. 2.68 \AA ; Nyburg & Faerman, 1985). The shortest Sn⋯F contacts are Sn(1)⋯F(17) = 2.686 (7) and Sn(2)⋯F(28) = 2.735 (7) \AA . These are somewhat longer than the 2.663 (4) and 2.681 (4) \AA contacts observed in Sn(R_f)₂ (Grützmaier, Pritzkow & Edelmann, 1991).

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Structure of (2,2'-Bipyridine *N,N'*-dioxide)dichloro(methanol)copper(II), [Cu(bpyO₂)(MeOH)Cl₂]

BY M. KOMAN, P. BARAN AND D. VALIGURA

Department of Inorganic Chemistry, Slovak Technical University, CS-81237 Bratislava, Czechoslovakia

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Abstract. [CuCl₂(C₁₀H₈N₂O₂)(CH₄O)], *M_r* = 354.68, monoclinic, *P*2₁/*c*, *a* = 16.420 (5), *b* = 8.545 (2), *c* = 19.001 (4) Å, β = 90.30 (1)°, *V* = 2665.9 (11) Å³, *Z* = 8, *D_m* = 1.77, *D_x* = 1.767 g cm⁻³, λ(Cu *K*α) = 1.54178 Å, μ = 61.33 cm⁻¹, *F*(000) = 1432, room temperature, *R* = 0.0615, *wR* = 0.0638 for 4056 reflections with *I* ≥ 3σ(*I*). The crystal structure is formed by discrete [Cu(bpyO₂)(MeOH)Cl₂] complex molecules. The asymmetric unit contains two such molecules. The coordination polyhedron of each Cu^{II} atom is a highly distorted tetragonal pyramid defined by two Cl and three O atoms.

Introduction. Aromatic *N*-oxides such as 2,2'-bipyridine *N,N'*-dioxide (abbreviated to bpyO₂ throughout this paper) can exhibit a wide variety of bonding modes since they can act as both bridging and chelating ligands. We have recently synthesized and studied two isomeric dimeric [Cu₂(bpyO₂)₂Cl₄] complexes (Baran, Koman, Valigura & Mrozinski, 1991). The same synthetic route gives different products if the temperature or solvent mixture is altered. Thus we have now obtained single crystals of [Cu(bpyO₂)(MeOH)Cl₂] by addition of dioxane to the methanolic reaction mixture and have undertaken their X-ray diffraction analysis.

Experimental. Green prism-shaped crystals prepared from methanol/dioxane (1:2) solution of CuCl₂ with bpyO₂ in the appropriate stoichiometric ratio. Crystal dimensions 0.81 × 0.29 × 0.13 mm; density measured by flotation. Syntax *P*2₁ diffractometer; 15

reflections with 11.60 ≤ θ ≤ 20.43° used to determine lattice parameters; absorption and extinction ignored. Intensity measurements from θ–2θ scans carried out for 0 ≤ 2θ ≤ 100°; *h*, *k*, *l* range: *h* – 18 to 18, *k* 0 to 10, *l* 0 to 22. Two reflections re-estimated after every 98 measurements decreased in intensity by 15% during the course of the experiment; 4056 independent reflections with *I* ≥ 3σ(*I*) (1750 unobserved reflections); 439 refined parameters. Cu-atom positions from Patterson function, other non-H atoms from Fourier syntheses; H atoms from difference syntheses. Anisotropic full-matrix refinement for non-H atoms (H-atom refinement isotropic) based on *F*. *R* = 0.0615, *wR* = 0.0638, *S* = 1.64; *w* = *k*/[σ²(*F_o*) + *g*(*F_o*)²], *k* = 16.7547, *g* = 0.000257; |Δρ| ≤ 0.71 e Å⁻³; (Δ/σ)_{max} in final least-squares cycle 1.40. Calculations performed with *SHELX76* program system (Sheldrick, 1976); scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV).

Discussion. Final coordinates of the non-H atoms are listed in Table 1* and selected interatomic distances and bond angles are in Table 2. The molecular structure and atomic numbering are shown in Fig. 1.

* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54373 (28 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.